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EMISSIONS FROM BURNING CABINET MAKING SCRAPS

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EMISSIONS FROM BURNING CABINET MAKING SCRAPS

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ABSTRACT

The object of this project was to make an initial determination of differences in emissions when burning ordinary cordwood compared to kitchen cabinet making scraps. The tests were performed in an instrumented woodstove testing laboratory on a stove which simulated units observed in use at a kitchen cabinet manufacturer's facility. A series of three test burns were made using a stove made from a 55 gallon drum and a kit sold for that purpose. The first test burn used seasoned oak cordwood fuel while the second test burn used particle board scraps for fuel. The third test burn used Formica© faced particle board scraps for fuel. The scraps for tests two and three were obtained from a kitchen cabinet manufacturer in Vermont. In general the cordwood produced lower emissions of the heavier molecular weight organic compounds. There were significant differences in burnrate between the tests which introduced some uncertainty in interpreting the analytical results.

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SECTION 1

INTRODUCTION

Under the direction of Control Technologies Center (CTC), Acurex Environmental Corporation was contracted to characterize the emissions generated by the combustion of scrap wood composite products at small cabinet manufacturing companies in Vermont. The scrap is burned to heat the facilities and reduce the companies' waste disposal costs. The state of Vermont asked for assistance after receiving complaints from citizens about visible emissions and odors emanating from the two facilities.

One of the Vermont facilities (facility A) specializes in manufacturing countertops. The laminated surface composite wood material is received ready-to-use and is then cut to specifications. Four cylindrical steel furnaces with 0.28 m^3 (10 ft^3) combustion chambers are used for burning scrap. Draft on the furnaces is regulated manually and the fuel is fed manually as needed. The smoke has a burning plastic odor which is stronger at startup and refueling. Complaints have come mainly from passers-by.

Scrap produced by the other facility (facility B) consists of saw dust, small pieces of particle board, and plywood. The furnaces have primary and secondary air controls. Scrap chunks are fed by hand but saw dust is fed automatically.

Composite woods contain several types of phenolic resins including phenol-formaldehyde resin and melamine resin[1]. The chief components of phenolic resins are formaldehyde, acetaldehyde, and phenol. Characteristics of these resins are resistance to moisture, solvents, and heat up to 200 °C.

They are also dimensionally stable, sound absorbent, and noncombustible. Chief components of melamine resin are formaldehyes, phenols, and cyano-benzenes.

SECTION 2

EXPERIMENTAL APPROACH

2.1 PROJECT DESCRIPTION

This project's goal was to characterize emissions from the burning of common kitchen counter top scrap material (plain particle board and particle board laminated with Formica©). The conditions at Vermont facility A were emulated. To reduce expenditures, sampling was performed in the woodstove testing laboratory of the U.S. Environmental Protection Agency/Air and Energy Engineering Research Laboratory (EPA/AEERL) in the Environmental Research Center (ERC). Three varieties of wood were burned, cordwood (virgin wood), particle board, and Formica© board (Formica©-covered particle board). Cordwood was sampled for comparison purposes. Both composite woods were provided by facility A. Only one test was performed per day, lasting 2-5.3 hours. Again, to reduce expenditures, only one sample was planned for each fuel.

Acurex Environmental performed all sampling activities, and prepared and analyzed all filter and XAD-2 samples. Non-volatile organic compounds (NVOC) were analyzed by gravimetric methodologies (GRAV). Semi-volatile organic compounds (SVOC) were analyzed by gas chromatograph/ flame ionization detection (GC/FID) and gas chromatograph/ mass spectroscopy (GC/MS). Samples for volatile organic compounds (VOC) and aldehydes were transferred to EPA/AREAL for analysis. Table 2-1 presents the sampling and analysis responsibilities.

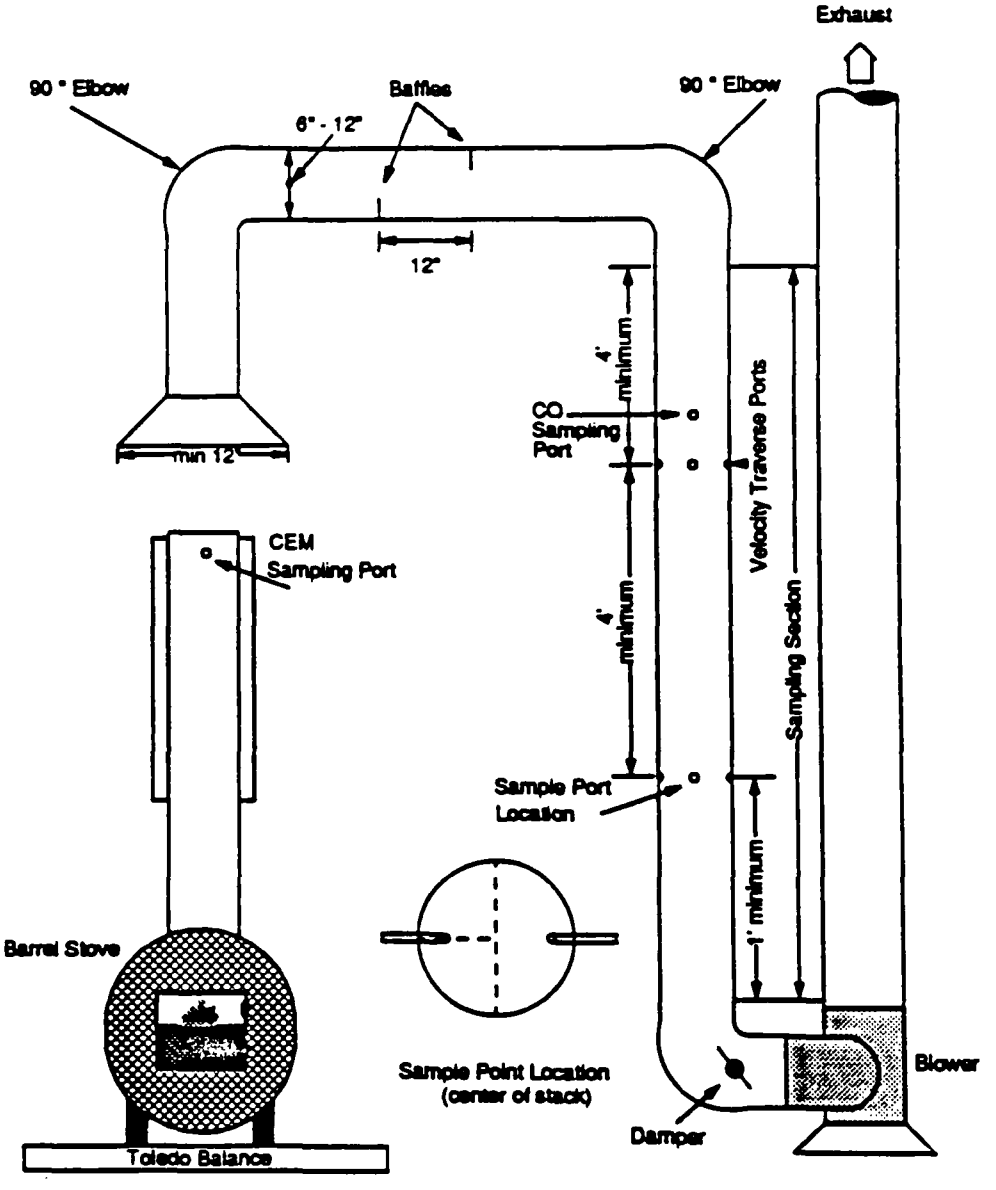
TABLE 2-1. SAMPLING AND ANALYSIS RESPONSIBILITIES

	Acurex Environmental	Acurex Environmental/AEERL	AREAL
Filter and XAD-2 preparation	X		
Sampling		X	
CEM operation		X	
Aldehyde analysis			X
VOC analysis			X
GRAV analysis	X		
TCO analysis	X		
GC/MS analysis	X		

2.2 EXPERIMENTAL APPARATUS

Sampling was performed according to EPA method 5G, with modifications to include the collection of samples for chemical analysis. The wood was burned in a barrel stove constructed from a 0.28 m^3 (55-gal) steel drum and a kit purchased from McMaster Carr, Inc. This stove provided the manual fuel feed and air control used at facility A. The stove was mounted on a Toledo electronic balance with a weight capacity of 300 kg to measure fuel additions and monitor short-term fuel consumption. An insulated 0.152 m (6 in) diameter stack ran 3.66 m (12 ft) from the top of the stove to a dilution tunnel (Figure 2-1). Stack exhaust enters the head of the dilution tunnel at the dilution bell. The bell draws in air to dilute the sample and isolate the mass borne by the scale from the dilution tunnel. The dilution process cools the sample to ambient temperature so that condensable gases (those analytes whose vapor pressures are low at ambient temperature) can be collected with a filter.

Samples were taken from two sample ports near the base of the dilution tunnel. Aldehydes were drawn from one sampling port and SVOCs were drawn from the other. VOCs were drawn from a line between the filter and the XAD-2 cartridge. NVOCs were collected from the SVOC sampling train. Figure 2-2 illustrates the sampling trains.



1" = 2.54 cm

Figure 2-1. Barrel stove and dilution tunnel.

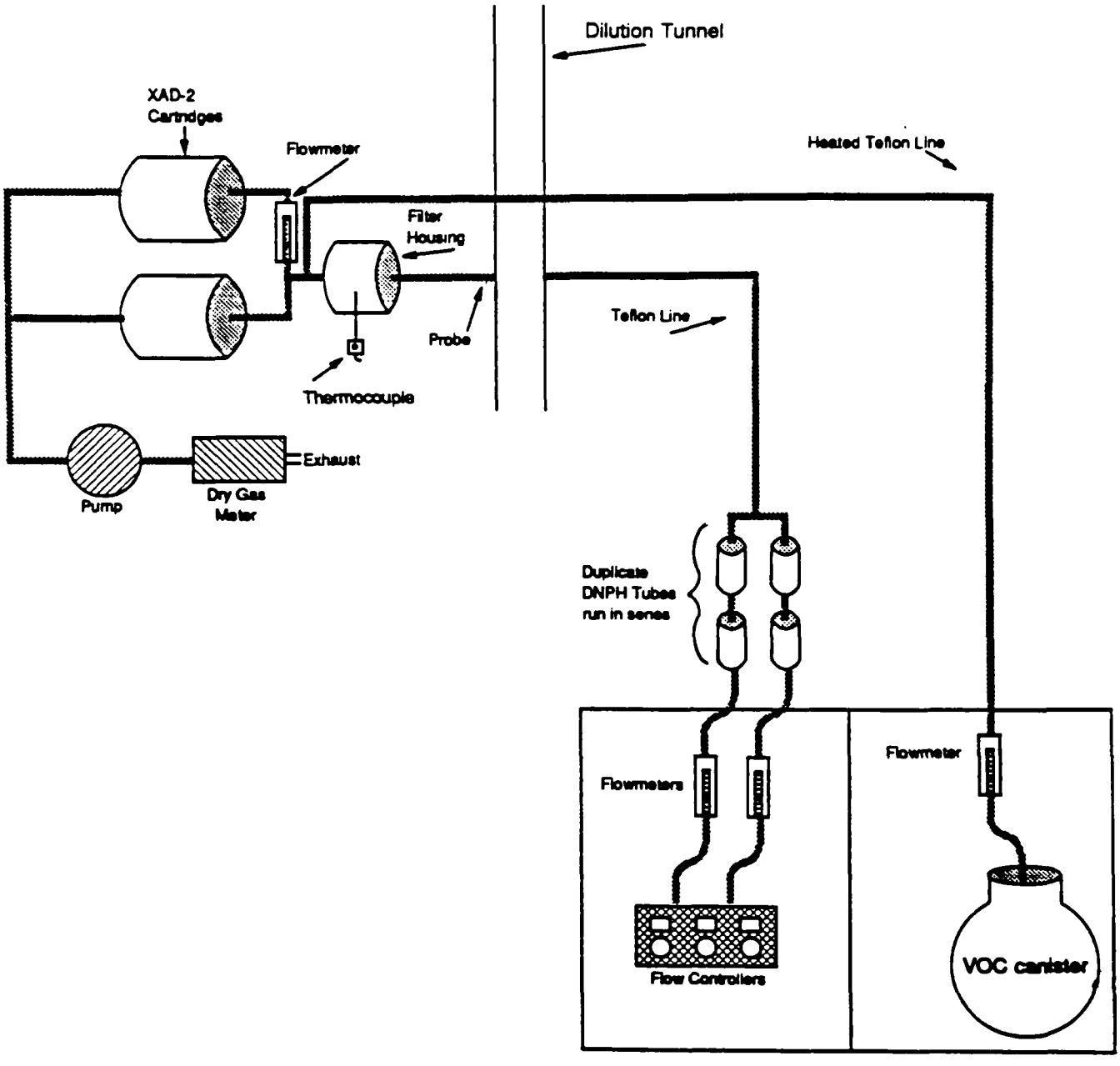


Figure 2-2. Sampling trains.

VOCs were collected in an evacuated stainless steel canister via a heated line as a side stream between the glass fiber filters and the XAD-2 cartridges. VOC collection post-filter ensures a particulate-free sample. A critical orifice at the inlet of the canister controlled the flow so that a time-averaged sample was collected. A dry gas meter determines the total sample volume collected. These canisters were delivered to Acurex Environmental ready for sample collection by EPA/AREAL and returned for analysis.

The aldehyde sampling train consisted of a teflon line that ran to two pairs of dinitrophenylhydrazine (DNPH)-impregnated tubes parallel to the flow and split equally between the pairs. A flow meter at the end of both pairs of tubes monitored their respective flows. Aldehydes react with the DNPH to provide non-volatile derivatives that are ready for analysis by high performance liquid chromatography (HPLC). The DNPH tubes were delivered to Acurex Environmental by AREAL ready for sample collection and were returned for analysis.

A modification to the method 5G wood heater sampling protocol was used to sample SVOCs and NVOCs. This sampling train consisted of two filters run in series followed by a pair of XAD-2 cartridges in parallel, with the flow split equally between them. Equal flow was maintained by a flow meter and control valve placed before one of the XAD-2 cartridges and a control valve placed before the other cartridge. The total flow was monitored by a dry gas meter at the end of the sampling train.

Continuous emission monitor (CEM) measurements and temperature readings were collected from the stack 2.8 m (8 ft) from the top of the balance.

2.3 EXPERIMENTAL METHODS AND PROCEDURES

2.3.1 Preparation for Sampling

Filters were rinsed in dichloromethane, desiccated for at least 24 h, tared, and stored in petri dishes in the desiccator until sampling.

The XAD-2 resin was cleaned and quality control checked according to AEERL/ROP No. 40 (Appendix A). Approximately 170 g of cleaned XAD-2 were placed into each stainless steel canister, sealed in a Teflon bag, and stored in the freezer until sampling.

2.3.2 Sampling Facility Operation

Each test was started with a bed of hot cordwood coals. Sampling data was recorded at 10-min intervals by the operator and consisted of balance readings, barometric pressure, and flow data for the sampling trains. Barometric pressure was recorded once per day. Interruptions for fuel additions were recorded.

After each test, the glass sampling probe connecting the stack and the filter was rinsed with acetone. The probe rinse is the rinsate collected by this operation.

Ash samples were collected from the barrel stove and stored in glass sample jars with Teflon® sealed lids at the conclusion of each test.

SVOCs and NVOCs were collected at an average flow rate of 0.799 m^3/h. The flow rate was calculated from a dry gas meter at the end of the sample train and the elapsed time.

Table 2-2 summarizes the sampling conditions for the three tests.

TABLE 2-2. ACTUAL SAMPLING CONDITIONS

Date	10/5/90	10/10/90	10/11/90
Fuel type	cordwood	particle board	Formica© board
Sampling time (h:min)	5:23	2:13	5:21
Avg. fuel consumption (kg/h)	5.39	8.10	4.71
Dilution factor	6.3	22.6	23.5
Stack gas flow rate (m^3/h)	9.11	0.85	0.82
Total gas (m^3)	49.02	1.89	4.38
Total fuel consumption (kg)	28.9	19.6	20.5
Number of fuel charges	3	3	5

2.3.3 Aldehyde Analysis

Roy B. Zweidinger of the EPA/AREAL supplied DNPH tubes for sampling and provided the aldehyde analyses after sampling was finished.

Aldehydes were analyzed by HPLC in the laboratories of Roy Zweidinger of EPA/AREAL by the procedures established in that laboratory. Each tube was analyzed individually. The four tubes

collected from each burn provided QA checks on the analysis and sample collection. Analysis of the back tubes detected the presence of break-through during sample collection. Comparing results from the parallel sample collections detected questionable results caused by such factors as tube overload, clogging, etc.

2.3.4 Volatile Organics Analysis

Bob Seila of EPA/AREAL provided Summa canisters for sampling and performed the GC/FID analyses of VOCs by the procedures established in his laboratory. An aliquot of gas from the Summa canister was injected. Compound identification was based on comparing retention time to a library of well-characterized standard compounds. For identified compounds, quantification was performed from stored calibrations. Where identification was not possible, an averaged response factor was used.

2.3.5 CEM Data

Continuous emission monitors collected data for total hydrocarbon (THC), carbon dioxide (CO_2), carbon monoxide (CO), and oxygen (O_2) concentration in the stack, as well as the CO concentration in the dilution tunnel. CO and CO_2 were monitored with an 880 Rosemount Analytical instrument and O_2 was monitored with a 755 Rosemount Analytical instrument. THCs were monitored with a VE7 JUM Engineering instrument. All CEMs were calibrated with three concentrations of span gas appropriate to each instrument. Thermocouples located in the stack and dilution tunnel were used to monitor temperature. Data were recorded at 1-min intervals, transferred to a Lotus spreadsheet, and then stored to disk.

2.3.6 Sample Extraction

After sampling, the filters were placed back into petri dishes and stored in a desiccator. Filters were desiccated for a minimum of 24 h then weighed to determine the total sample capture before extraction. Both filters for each test were divided in half. Half of the front filter and half the back filter were combined and extracted with dichloromethane by ultra sonic extraction. The two remaining halves were archived. The filter halves from a test were placed in a Level 1-cleaned beaker[2]. One hundred mL of reagent grade dichloromethane was added to the beaker which was sufficient to completely submerge the filters. An aluminum foil cover was placed over the mouth of the beaker and the beaker

was placed into an ultrasonic water bath. Liquid level in the bath was shallow enough to allow the beaker to sit firmly on the bottom. The ultrasonic bath was then run for 15 min. After sonicating, the dichloromethane was poured off into a collection flask. These steps were repeated three times to extract 400 mL of dichloromethane.

After sampling, the XAD-2 cartridges were resealed in Teflon® bags and stored in a freezer until extraction. One of each pair of XAD-2 cartridges was extracted by pump-through elution as described in ROP/AEERL No. 41 (Appendix A), the other was archived.

Before extraction, the ash samples were crushed with a mortar and pestle and passed through a 16 mesh sieve. Ash samples were extracted with dichloromethane in a soxhlet extraction apparatus as described in ROP/AEERL No. 22 (Appendix A). All remaining ash was archived.

All dichloromethane extracts were concentrated using a Kudema-Danish apparatus as described in AEERL/ROP No. 41. Concentration was stopped at the first evidence of saturation and the extract was made up to a known volume. All extracts were stored in a freezer after analysis.

2.3.7 Gravimetric Analysis

NVOCs were collected in the probe rinse, filters, and XAD-2 and analyzed by gravimetric methodology according to AEERL/ROP No. 12 (Appendix A). Ash samples were also analyzed by GRAV but all samples were below quantifiable limits.

Each sample was analyzed in duplicate and the reported result is the average of these determinations. A slight deviation from the protocol was implemented to conserve sample and time. A 0.25 mL aliquot of sample was added to each pan rather than the standard 1.0 mL. Each GRAV test included the analysis of blank samples to detect contamination by laboratory particulate.

Balance data were transferred directly to a computer spreadsheet by way of an RS-232 interface and Lotus Measure. This change eliminated data transfer and arithmetic errors. QC tests are built into the spreadsheet to ensure valid reporting of data. Any sample which fails these QC tests is repeated with additional weighings or fresh extract in new pans until all samples pass.

Detection limits were established at three times the smallest displayed unit of the balance (0.01 mg) and the quantifiable limit was five times the detection limit.

2.3.8 Total Chromatographable Organics Analysis

SVOCs were collected on XAD-2 cartridges and 11 cm glass fiber filters. The concentrated filter and XAD-2 extracts were then analyzed by GC/FID according to AEERL/ROP No. 13 (Appendix A). Ash extracts were also analyzed but contained no TCO mass. Individual peaks were not identified.

Each sample is analyzed in duplicate by direct injection GC/FID and the reported result is the average of these determinations. The first and last sample from each daily test is a QC check sample. If either QC check sample fails; the entire sample test is repeated after the problem is located and resolved. Any sample that fails the ROP's repeatability requirement is re-run with a fresh aliquot. Quantitation of individual compounds was not performed by GC/MS because it would have duplicated available information, in principle, from the GC/FID analysis at a high cost.

2.3.9 GC/MS Analysis

GC/MS was performed to identify compounds in both the XAD-2 and filter extracts. Compounds were identified by matching the retention times with a National Institute of Standards and Technologies mass spectral library. Quantitation of individual compounds was not performed.

2.3.10 Calculations

The quantity of SVOCs collected during the cordwood test was 0.069 g. During the test, 4.33 m^3 were sampled from the dilution tunnel. The sample was drawn through two XAD-2 cartridges with equal flow through them. The stack flow rate was 57.4 m^3/h and the burn rate was 5.39 kg/h.

Specifications for the average gaseous concentration in the stack was as follows:

- (0.069 g*2/ 4.33 m^3)6.3 = 0.20 g/m^3
- Emissions/h = (0.20 g/m^3)(57.4 m^3/h) = 11.48 g/h
- Emissions/kg of fuel = (11.48 g/h)/(5.39 kg/h) = 2.13 g/kg

Filter capture is the difference between presampling and post-sampling filter weights. The total capture is the sum of the filter capture, XAD-2, and the probe rinse. SVOC is the sum of the TCOs for the XAD-2 and filter extracts. Extractable NVOC is the sum of the GRAV for the XAD-2 and filter extracts.

SECTION 3

PRESENTATION OF RESULTS

Table 3-1 summarizes the CEM data. Table 3-2 describes the totals of CEMs, VOCs, SVOCs, and NVOCs as a function of gaseous concentration, emission rate, and emission/fuel mass consumed. VOC data for the cordwood and composite woods are described in Table 3-3. Tables 3-4 through 3-6 list the compounds identified by GC/MS in each of the three wood types. Table 3-7 presents all the compounds identified in all three wood types for ease of comparison. Table 3-8 compares some GC/MS results by compound class.

Figures 3-1 through 3-10 are MS chromatographs. Figures 3-1 through 3-3 are of XAD-2 extracts, Figures 3-4 through 3-6 are filter extracts, and Figures 3-7 through 3-10 are subtractions of cordwood wood from composite wood. Figures 3-11 through 3-15 compare the CEM data from the three fuels. Figures 3-16 through 3-18 relate the CEM data for each of the three fuels.

TABLE 3-1. CEM DATA SUMMARY

	Cordwood	Particle Board	Formica® Board
O_2 (%) minimum	0.76	0.37	1.01
average	8.98	10.55	12.02
std.dev.	4.41	4.71	3.93
maximum	14.94	16.04	16.96
CO (ppm) minimum	1328	1415	1022
average	17832	19161	16548
std. dev.	6563	6757	4861
maximum	33102	34263	27128
CO_2 (%) minimum	6.45	6.61	3.55
average	11.93	10.54	9.37
std. dev.	3.48	3.63	3.12
maximum	18.01	18.27	17.77
THC (ppm) minimum	196	157	1
average	1123	1048	739
std. dev.	1274	1415	1044
maximum	5102	5987	10071
TEMP (C) minimum	348	349	311
average	641	628	567
std. dev.	231	291	202
maximum	1074	1262	1135

TABLE 3-2. SUMMARY OF EMISSION DATA FOR ALL FUELS

TABLE 3-2. Summary of Emission Data for All Fuels

Emission Data for Cordwood, Particle Board, and Formica Board Expressed as Gaseous Concentration (g/m3)

	cordwood	particle board	formica board
Total Capture	0.75	3.98	4.26
Filter Capture	0.41	2.80	2.67
Non-volatile Extractable Organics	0.31	1.34	1.64
Semi-volatile Organics	0.20	0.36	0.80
Volatile Organics	5.26	63.89	
Total Hydrocarbons (ppm)	2.21	2.11	1.46
CO (ppm)	22.29	24.36	20.74
CO2 (%)	11.9	10.5	9.4

Emission Data for Cordwood, Particle Board, and Formica Board Expressed as Emission Rate (g/h)

	cordwood	particle board	formica board
Total Capture	43.23	76.46	81.81
Filter Capture	23.42	53.91	51.28
Non-volatile Extractable Organics	17.79	25.77	31.52
Semi-volatile Organics	11.48	6.92	15.38
Volatile Organics	302.09	1228.63	
Total Hydrocarbons	126.69	40.52	28.08
CO	1279.52	468.43	398.63

Emission Data for Cordwood, Particle Board, and Formica Board Expressed as emission per fuel mass (g/kg)

	cordwood	particle board	formica board
Total Capture	8.02	9.44	17.37
Filter Capture	4.34	6.66	10.89
Non-volatile Extractable Organics	3.30	3.18	6.69
Semi-volatile Organics	2.13	0.85	3.26
Volatile Organics	56.05	151.68	
Total Hydrocarbons	23.50	5.00	5.96
CO	237.39	57.83	84.63

TABLE 3-3. GC/FID VOLATILE ORGANIC COMPOUND ANALYSIS (cont.)

compound	retention time	combined peaks	mg/m3 cordwood	combined peaks	mg/m3 particle board	mg/hr cordwood	mg/hr particle board	mg/kg cordwood	mg/kg particle board
unknown	2.234 to 2.349	(2)	0.85			48.71		9.04	
ethylene	2.497		19.73		28.70	1,132.61	551.91	210.13	68.14
acetylene	3.080		8.57		25.32	492.07	486.98	91.29	60.12
Ethane	3.592				1.91		36.68		4.53
propene	4.104		9.99		3.13	573.28	60.29	106.36	7.44
propane	4.235		3.72		0.58	213.32	11.24	39.58	1.39
unknown	4.437 to 6.470	(6)	2.84	(3)	1.66	162.91	32.00	30.22	3.95
iButane	6.73		0.20			11.69		2.17	
unknown	7.020 to 8.058	(4)	5.10	(3)	4.65	292.99	89.46	54.36	11.04
nButane	8.245		0.49			28.24		5.24	
unknown	8.594		0.14			7.81		1.45	
t-2-Butene	8.755		0.74		1.22	42.36	23.51	7.86	2.90
unknown	9.123		0.05			2.69		0.50	
1&2 Butyne	9.218		0.10			5.75		1.07	
c-2-Butene	9.359		0.30			17.00		3.15	
unknown	10.283 to 12.069	(2)	1,125.96	(1)	443.00	64,631.89	8,519.59	11,991.07	1,051.80
C5 Olefin	13.073				33,278.80		640,005.81		79,013.06
C6 Paraffin	13.58		2,341.95		21,028.81	134,431.75	404,418.36	24,940.96	49,928.19
unknown	13.837		1,037.40			59,548.51		11,047.96	
C6 Olefin	13.981				5,661.91		108,887.72		13,442.93
C6 Olefin	14.195				3,364.83		64,711.26		7,989.04
unknown	14.274 to15.806	(4)	640.88	(2)	15.36	36,787.30	295.39	6,825.10	36.47
C6 Olefin	15.915		5.88			337.56		62.63	
nHexane	16.148		0.04			2.46		0.46	
Chloroform	16.257		2.26			129.65		24.05	
C6 Olefin	16.414		0.06			3.62		0.67	
unknown	16.675		0.16			9.20		1.71	
C6 Olefin	16.85		0.04			2.51		0.47	
unknown	17.048 to 17.205	(2)	0.03			1.59		0.29	
2,2,3 TriMeBut	17.336		0.03		0.18	1.70	3.54	0.32	0.44

( ) indicates the number of peaks found within that retention time window

TABLE 3-3. GC/FID VOLATILE ORGANIC COMPOUND ANALYSIS (cont.)

compound	retention time	mg/m3 combined peaks	cordwood	combined peaks	particle board	mg/hr cordwood	particle board	mg/kg cordwood	particle board
Benzene	17.821		26.23		16.53	1,505.85	317.86	279.38	39.24
3,3 DiMePenta	17.997		0.21			12.04		2.23	
CycloHexane	18.12		0.04			2.29		0.43	
unknown	18.203		0.03			1.85		0.34	
2MeHexane	18.407		0.02			1.38		0.26	
unknown	18.512		0.01			0.65		0.12	
C7 Paraffin	18.601		0.11			6.09		1.13	
3MeHexane	18.688		0.02			1.25		0.23	
unknown	18.751		0.05			2.85		0.53	
1,3 DiMeCyPe	18.93		0.01			0.68		0.13	
Tricloroeth	19.072		0.03			1.95		0.36	
2,2,4 TrMePent	19.135		0.09			5.04		0.93	
C7 Olefin	19.202		0.10			5.48		1.02	
C7 Olefin	19.297		0.19			11.14		2.07	
nHeptane	19.496		0.07			4.12		0.76	
C8 Olefin	19.637		0.01			0.80		0.15	
C8 Olefin	20.034		0.02			0.91		0.17	
unknown	20.337		0.18			10.05		1.86	
2,4 DiMeHexan	20.583		0.12			7.08		1.31	
C8 Olefin	20.738		0.03			1.90		0.35	
Toluene	21.298		5.31		3.20	304.59	61.59	56.51	7.60
2Me3EtPenta	21.488		0.03			1.46		0.27	
unknown	21.668		0.35			19.95		3.70	
3EtHexane	21.831		0.02			1.13		0.21	
unknown	22.175		0.31			17.78		3.30	
1t2DiMeCyHe	22.529		0.05			3.13		0.58	
C9 Paraffin	22.618		0.06			3.50		0.65	
Percloroeth	22.632				0.30		5.77		0.71
C9 Paraffin	22.752				0.55		10.62		1.31
C9 Olefin	22.836		5.14			294.87		54.71	

( ) indicates the number of peaks found within that retention time window

TABLE 3-3. GC/FID VOLATILE ORGANIC COMPOUND ANALYSIS (cont.)

compound	retention time	combined peaks	mg/m3 cordwood	combined peaks	particle board	mg/hr cordwood	particle board	mg/kg cordwood	particle board
2,3,5 TriMeHex	22.993		0.02			1.33		0.25	
unknown	23.125		0.03			1.98		0.37	
2,4 DiMeHepta	23.186		0.09			4.95		0.92	
4,4 DiMeHepta	23.302		0.05			2.83		0.52	
unknown	23.493		0.01			0.40		0.08	
1,1,3 TriMCyhe	23.693		0.05			2.87		0.53	
C9 Olefin	23.824		0.08			4.37		0.81	
EtBenzene	23.996		0.71		0.38	40.89	7.22	7.59	0.89
unknown	24.280 to 24.588	(2)	0.76			43.46		8.06	
C9 Paraffin	24.653		0.02			1.05		0.20	
C9 Paraffin	24.828				1.07		20.62		2.55
unknown	24.842		0.79			45.40		8.42	
Nonene-1	24.958		0.33			18.84		3.49	
C9 Olefin	25.167		0.01			0.49		0.09	
C9 Paraffin	25.299		0.03			1.87		0.35	
unknown	25.387		0.04			2.43		0.45	
C9 Olefin	25.516		0.04			2.40		0.44	
C9 Paraffin	25.691		0.01			0.63		0.12	
2,2 DiMeOctan	25.77		0.10			6.00		1.11	
unknown	25.921		0.07			3.85		0.71	
C10 Paraffin	26.093		0.02			1.37		0.25	
C10 Olefin	26.254		0.90			51.48		9.55	
unknown	26.343				0.52		9.96		1.23
3,6 DiMeOctan	26.375		1.43			82.31		15.27	
C10 Paraffin	26.474		0.02			1.02		0.19	
unknown	26.551		0.08			4.63		0.86	
2,3 DiMeOctan	26.776				0.44		8.51		1.05
5 MeNonane	26.797		0.39			22.10		4.10	
2 MeNonane	26.948		0.05			2.79		0.52	
oEtToluene	27.15		0.04		0.73	2.56	13.97	0.48	1.72

( ) indicates the number of peaks found within that retention time window

TABLE 3-3. GC/FID VOLATILE ORGANIC COMPOUND ANALYSIS (cont.)

compound	retention time	mg/m3 combined peaks	mg/m3 cordwood	mg/m3 combined peaks	mg/m3 particle board	mg/hr cordwood	mg/hr particle board	mg/kg cordwood	mg/kg particle board
C10 Paraffin	27.237		0.13			7.23		1.34	
B-Pinene	27.41		0.14			8.04		1.49	
Decene-1	27.483		0.02		0.21	1.07	4.13	0.20	0.51
unknown	27.596		0.68			38.77		7.19	
nDecane	27.767		0.02			1.23		0.23	
C10 Paraffin	27.844		0.05			2.75		0.51	
secButBenz	28.019		0.08			4.45		0.83	
C10 Olefin	28.133		0.02			0.91		0.17	
C10 Olefin	28.188		0.03			1.51		0.28	
1,2,3 TriMeBe	28.29		0.28		0.30	16.12	5.76	2.99	0.71
C10 Paraffin	28.501		0.41			23.56		4.37	
C10 Aromat	28.592		0.04			2.27		0.42	
nButCyHexa	28.849				0.48		9.22		1.14
1,3 DiEtBenz	28.861		0.27			15.54		2.88	
unknown	28.986 to 29.103	(2)	0.48			27.84		5.16	
C10 Aromat	29.322		0.01			0.81		0.15	
C11 Paraffin	29.421		0.07			4.15		0.77	
C10 Aromat	29.548		0.04			2.11		0.39	
unknown	29.68		0.02			1.08		0.20	
C10 Aromat	29.743		0.03			1.80		0.33	
unknown	29.813		0.03			1.85		0.34	
C10 Aromat	29.975		0.10			5.49		1.02	
unknown	30.072 to 30.302	(3)	0.44			25.46		4.72	
C10 Aromat	30.551		0.02		0.21	1.37	4.08	0.25	0.50
unknown	30.664 to 30.755	(2)	1.21			69.25		12.85	
mDiiPropBe	31.218		0.07			3.83		0.71	
C11 Aromat	31.297		0.11			6.14		1.14	
C11 Aromat	31.472		0.10			5.48		1.02	
unknown	31.681		0.04			2.33		0.43	
C11 Aromat	31.781		0.02			1.07		0.20	

( ) indicates the number of peaks found within that retention time window

TABLE 3-3. GC/FID VOLATILE ORGANIC COMPOUND ANALYSIS (cont.)

compound	retention time	combined peaks	mg/m3 cordwood	combined peaks	mg/m3 particle board	mg/hr cordwood	mg/hr particle board	mg/kg cordwood	mg/kg particle board
unknown	31.915		0.10			5.49		1.02	
nDoDecene-	32.065		0.02		0.75	1.02	14.43	0.19	1.78
C11 Aromat	32.192		3.29			189.06		35.08	
nDodecane	32.287		0.01			0.50		0.09	
C11 Aromat	32.373		0.04			2.41		0.45	
C11 Aromat	32.496		0.06			3.21		0.60	
C12 Paraffin	32.603		0.02			1.21		0.23	
C12 Paraffin	32.707		0.12			6.73		1.25	
unknown	32.867		0.03			1.55		0.29	
C11 Aromat	33.037		0.42			24.00		4.45	
C11 Aromat	33.258		0.36			20.72		3.84	
unknown	33.388		0.03			1.56		0.29	
C11 Aromat	33.511		0.14			8.28		1.54	
unknown	33.761		0.01			0.44		0.08	
C12 Aromat	34.253		0.02			1.25		0.23	
unknown	34.479 to 35.139	(5)	0.45			25.92		4.81	
C13 Paraffin	35.351		0.02			1.00		0.19	
C13 Paraffin	35.623		0.04			2.04		0.38	
C12 Aromat	36.407		0.03			1.67		0.31	
C13 Aromat	36.564		0.01			0.77		0.14	
C13 Aromat	36.817		0.03			1.68		0.31	
Total			5,262.70		63,885.75	302,087.33	1,228,627.47	56,045.89	151,682.40

( ) indicates the number of peaks found within that retention time window

TABLE 3-4. CONDENSED SEMI-VOLATILE ORGANIC GC/MS RESULTS

Identified compounds found in combusted cordwood samples	
Retention time	Compound
4.59	2,4-hexadiene-1-ol
4.78	1,3-dimethyl-benzene
6.94	benzaldehyde
7.06	5-methyl-2-furancarboxaldehyde
7.72	phenol
9.30	4-methyl-phenol
9.77	3-methyl-phenol
9.94	4-methoxy-phenol
11.24	4-ethyl-benzemethenol
11.66	3,5-dimethyl-phenol
11.85	naphthalene
12.04	2-methoxy-4-methyl-phenol
12.32	1,2-benzendiol
13.37	3-methoxy-1,2-benzendiol
13.68	2-ethyl-2-methoxy-phenol
14.99	2,6-dimethyl-phenol
16.61	1,2,3-trimethyl-benzene
17.72	dibenzofuran
17.93	1-(2,6-dihydroxy-4-methoxyphenyl)-ethanone
21.03	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone
21.66	phenanthrene
23.28	benzo[c]cinnoline
24.00	2-hexadecanoic acid
24.20	2-phenol-naphthalene
25.33	pyrene
25.60	fluoranthene
26.07	benzo[b]naphtho[2,3-d]furan
29.05	decacene
29.12	benzo[ghi]fluoranthene
29.71	triphenylene
29.85	chrysene
32.05	1-eicosane
32.93	1,1-diphenyl-heptane

TABLE 3-5. PARTICLE BOARD SEMI-VOLATILE ORGANIC GC/MS RESULTS

Identified compounds found in combusted particle board samples	
Retention time	Compound
4.55	2,4-hexadiene-1-ol
4.97	ethyl-benzene
5.29	1,3,5,7-cyclotetrataene
7.64	4-hydroxyl-benzenesulfonic acid
8.86	1-propenyl-benzene
11.80	naphthalene
12.82	quinoline
16.60	acenaphthalene
17.35	2-naphthalenecarbonitrile
18.53	2,5-dimethyl-benzenebutanoic acid
21.65	phenanthrene
25.33	pyrene
25.60	fluoranthene
26.93	2-methyl-heptadecane
28.04	2-21-dimethyldocosane
28.59	1-phenanthrenecarboxycyclic acid
29.12	2-methyl-octadecane
29.63	1-methyl-octadecane
30.13	2-methyl-heptadecane
31.14	hexacosane
32.10	heptacosane
33.00	octacosane
33.97	nonacosane
35.09	tricontane
36.41	hentriacontane

TABLE 3-6. FORMICA© BOARD SEMI-VOLATILE ORGANIC GC/MS RESULTS

Identified compounds found in combusted Formica© board samples	
Retention time	Compound
4.82	2,4-hexadiene-1-ol
5.32	1,3,5,7-cyclotetrataene
6.04	3(2H)-pyridazinone
7.54	isocyano-benzene
7.88	4-hydroxyl-benzenesulfonic acid
8.89	1-propenyl-benzene
9.41	4-methyl-phenol
9.99	3-methyl-phenol
11.29	3,5-dimethyl-phenol
11.85	naphthalene
12.08	2-methoxy-4-methyl-phenol
13.71	4-ethyl-2-methoxy-phenol
13.93	1-methyl-naphthalene
14.34	1-(4-methoxyphenyl)-ethanone
15.11	2-methoxy-5-(1-propenyl)-phenol
17.37	2-naphthalenecarbonitrile
17.71	dibenzofuran
18.75	2,5-dimethyl-benzenebutanoic acid
24.17	6-propyl-tridecane
25.76	2-methyl-tetradecane
26.93	2-methyl-heptadecane
28.05	2,21-dimethyl-docosane
29.14	2-methyl-octadecane
30.15	2-methyl-heptadecane
31.15	hexacosane
32.10	heptacosane
33.00	octacosane
33.99	nonacosane
35.08	tricontane
36.44	hentriacontane

TABLE 3-7. SEMI-VOLATILE ORGANIC GC/MS RESULTS (combined)

		Cordwood	Particle	Formica[e]
1	2,4-hexadiene-1-ol	X	X	X
2	1,3-dimethyl-benzene	X		
3	benzaldehyde	X		
4	5-methyl-2-furancarboxaldehyde	X		
5	phenol	X		
6	4-methyl-phenol	X		X
7	3-methyl-phenol	X		X
8	4-methoxy-phenol	X		
9	4-ethyl-benzemethenol	X		
10	3,5-dimethyl-phenol	X		X
11	naphthalene	X	X	X
12	2-methoxy-4-methyl-phenol	X		X
13	1,2-benzendiol	X		
14	3-methoxy-1,2-benzendiol	X		
15	2-ethyl-2-methoxy-phenol	X		
16	2,6-dimethyl-phenol	X		
17	1,2,3-trimethyl-benzene	X		
18	dibenzofuran	X		X
19	1-(2,6-dihydroxy-4-methoxyphenyl)-ethanone	X		
20	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	X		
21	phenanthrene	X		
22	benzo[c]cinnoline	X		
23	2-hexadecanoic acid	X		
24	2-phenol-naphthalene	X		
25	pyrene	X		
26	fluoranthene	X		
27	benzo[b]naphtho[2,3-d]furan	X		
28	decacene	X		
29	benzo[ghi]fluoranthene	X		
30	triphenylene	X		
31	chrysene	X		
32	1-eicosane	X		
33	1,1-diphenyl-heptane	X		
34	ethyl-benzene		X	
35	1,3,5,7-cyclotetrataene		X	X
36	4-hydroxyl-benzenesulfonic acid		X	X
37	1-propenyl-benzene		X	X
38	quinoline		X	
39	acenaphthalene		X	
40	2-naphthalenecarbonitrile		X	X
41	2,5-dimethyl-benzenebutanoic		X	X
42	2-methyl-heptadecane		X	
43	2-21-dimethyldocosane		X	X
44	1-phenanthrenecarboxycyclic acid		X	
45	2-methyl-octadecane		X	X
46	1-methyl-octadecane		X	X
47	2-methyl-heptadecane		X	X
48	hexacosane		X	X
49	heptacosane		X	X
50	octacosane		X	X
51	nonacosane		X	X
52	tricontane		X	X
53	hentriacontane		X	X
54	3(2H)-pyridazinone			X
55	isocyano-benzene			X
56	4-ethyl-2-methoxy-phenol			X
57	1-methyl-naphthalene			X
58	1-(4-methoxyphenyl)-ethanone			X
59	2-methoxy-5-(1-propenyl)-phenol			X
60	6-propyl-tridecane			X
61	2-methyl-tetradecane			X

TABLE 3-8. CHEMICAL GROUPS OF GC/MS IDENTIFIED COMPOUNDS

	Cordwood	Particle Board	Formica® Board
Oxygenated	20/33 61%	4/22 18%	11/30 37%
Conjugated	29/33 88%	11/22 50%	17/30 57%
Fully saturated	0/33 0%	10/22 45%	12/30 40%

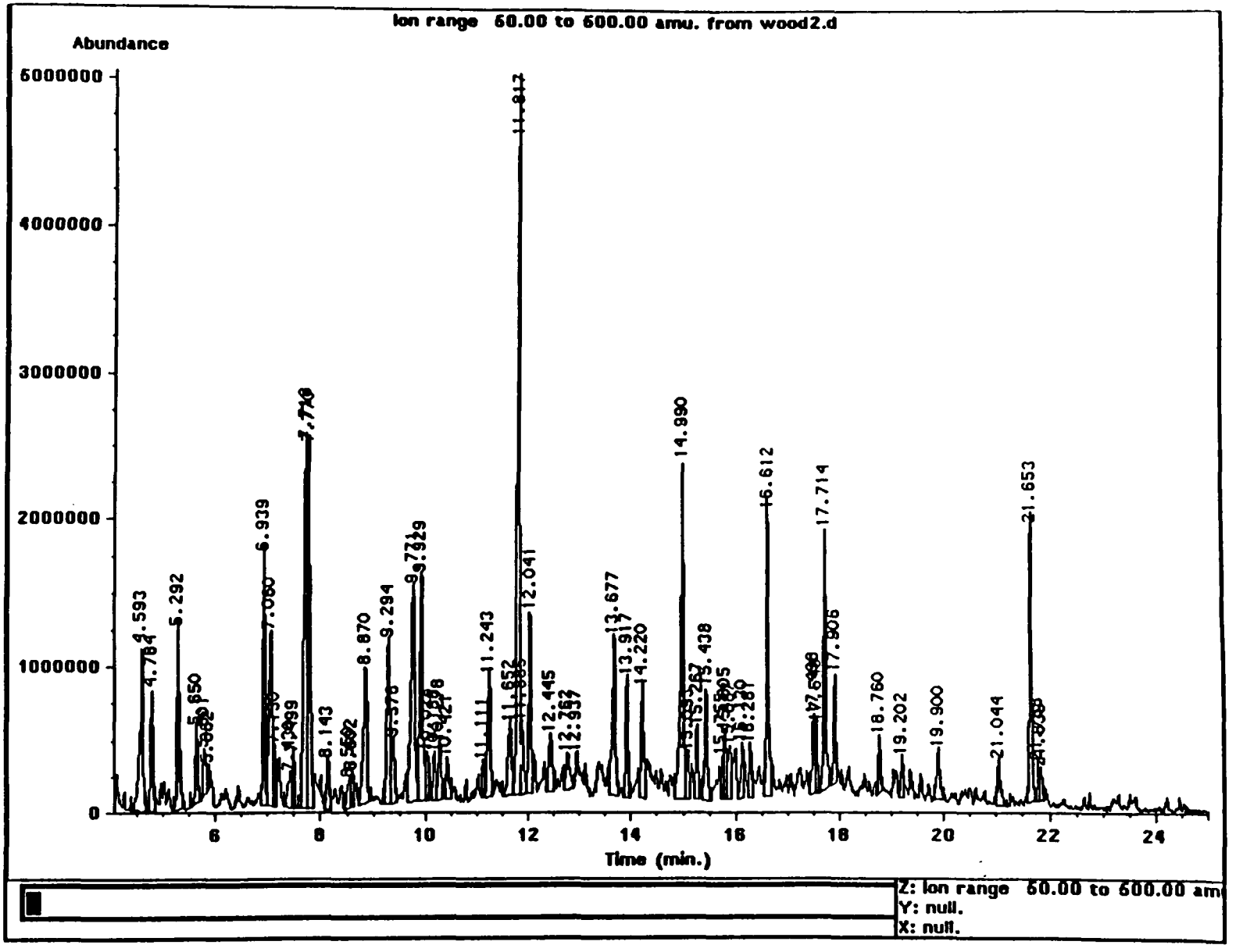


Figure 3-1. Mass spec chromatograph of cordwood sample extracted from XAD-2 resin.

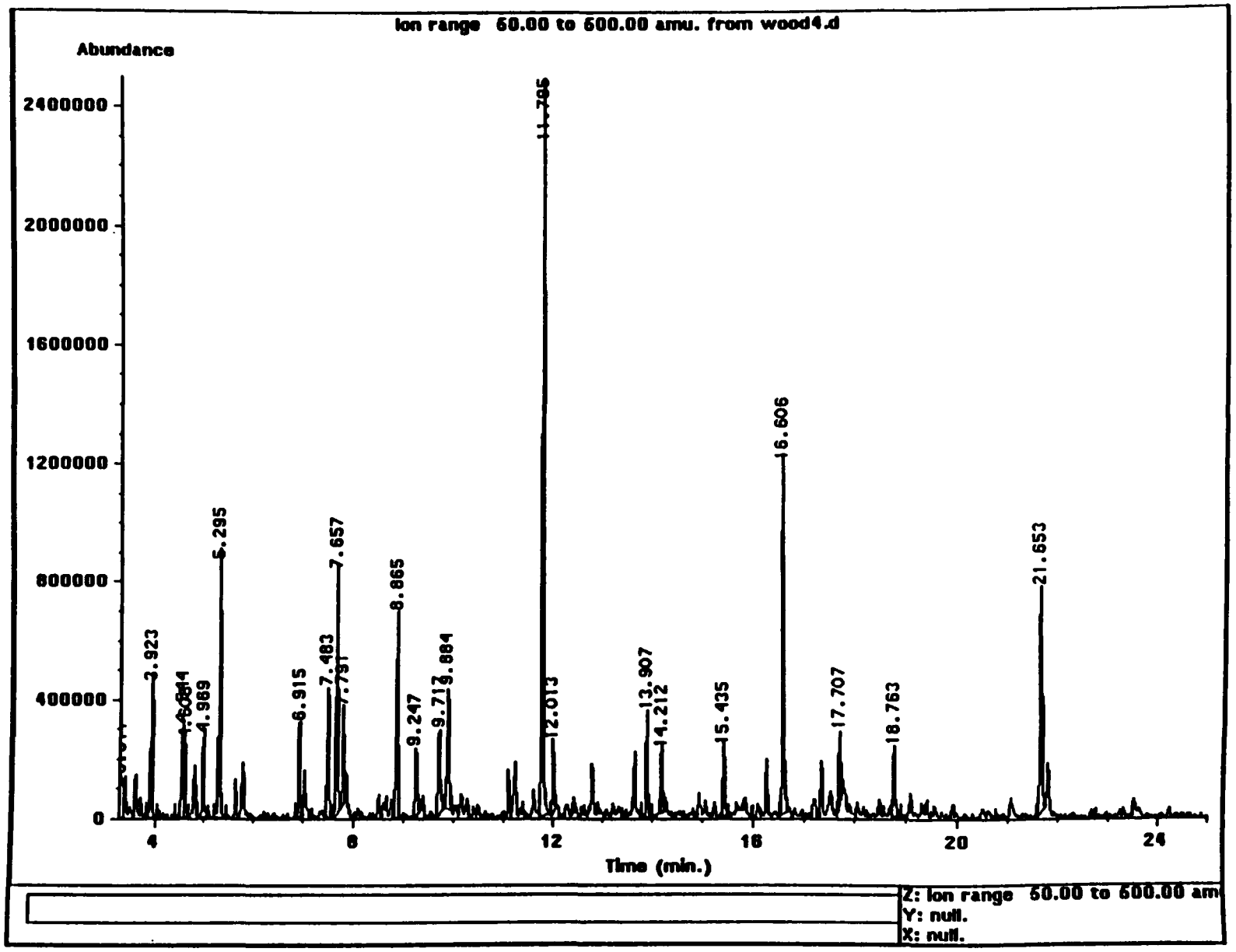


Figure 3-2. Mass spec chromatograph of particle board sample extracted from XAD-2 resin.

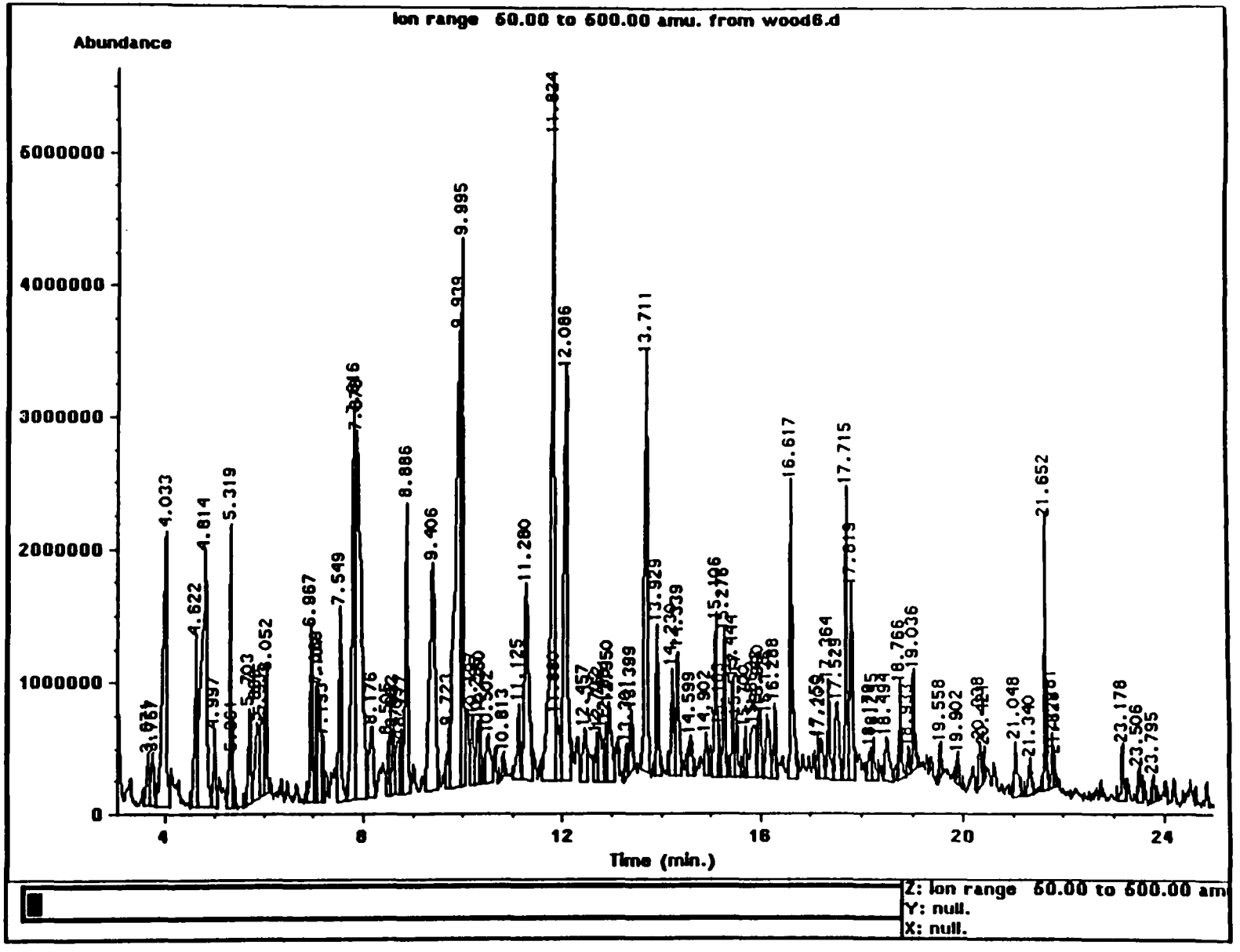


Figure 3-3. Mass spec chromatograph of Formica© board sample extracted from XAD-2 resin.

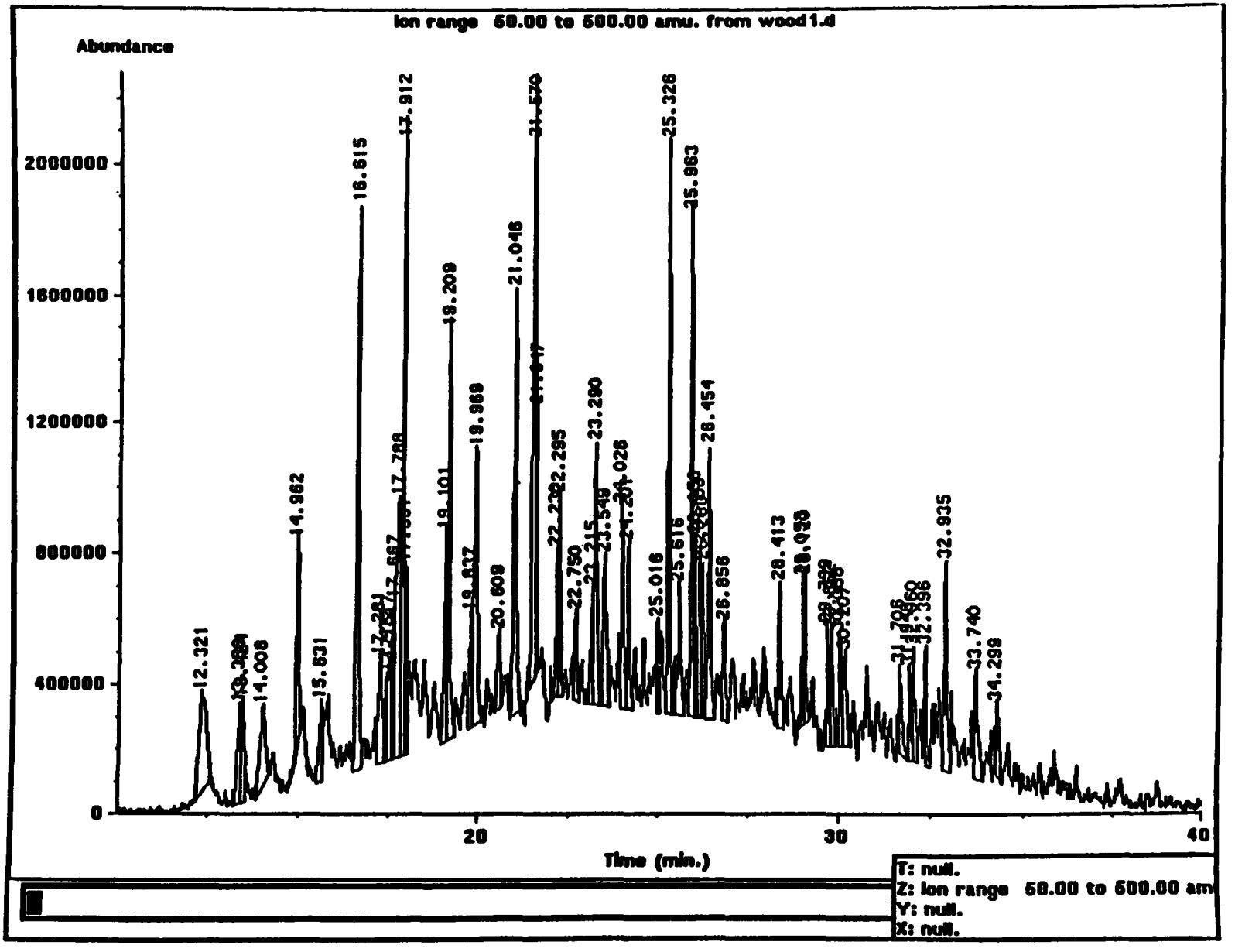


Figure 3-4. Mass spec chromatograph of cordwood sample extracted from quartz fiber filter.

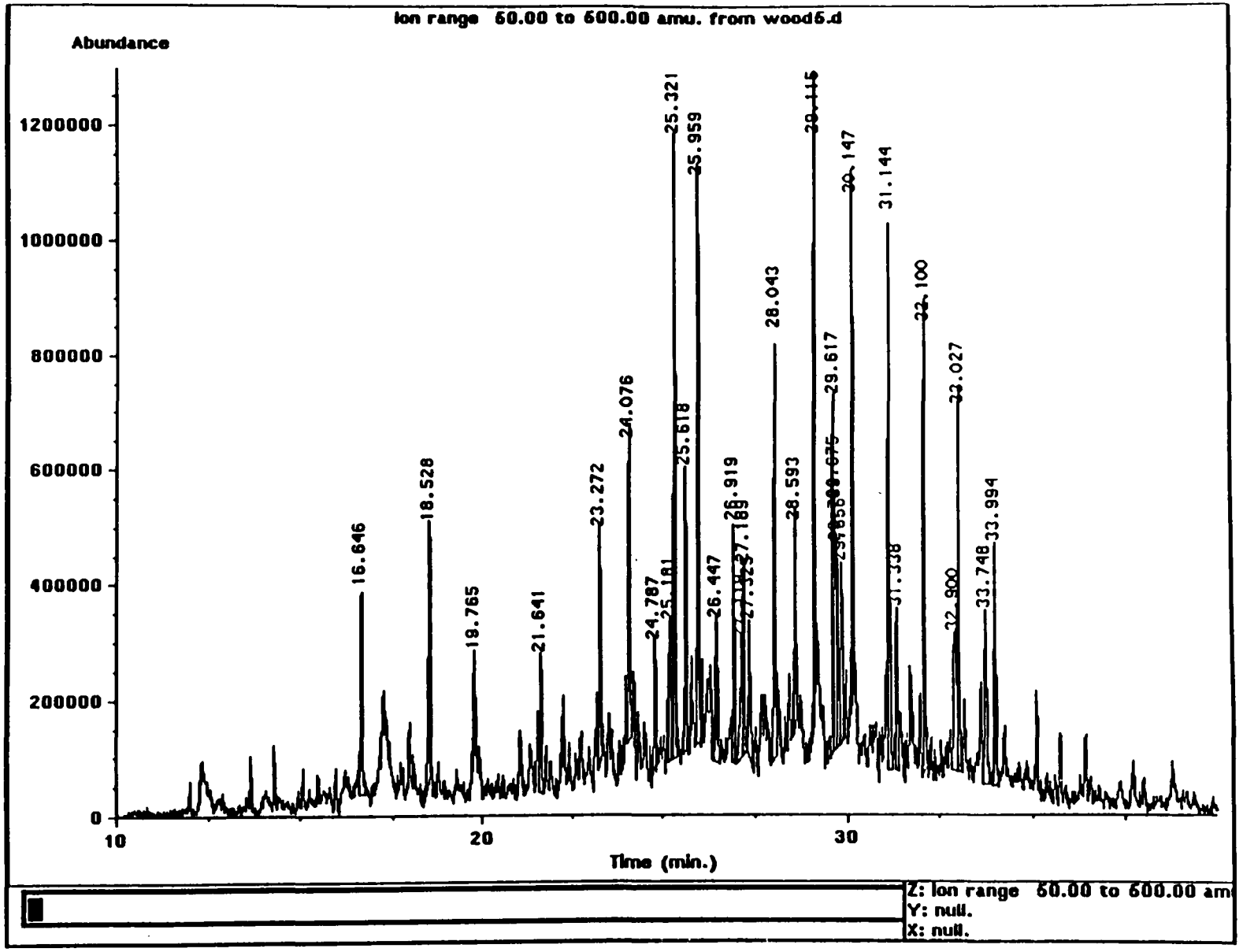


Figure 3-5. Mass spec chromatograph of particle board sample extracted from quartz fiber filter.

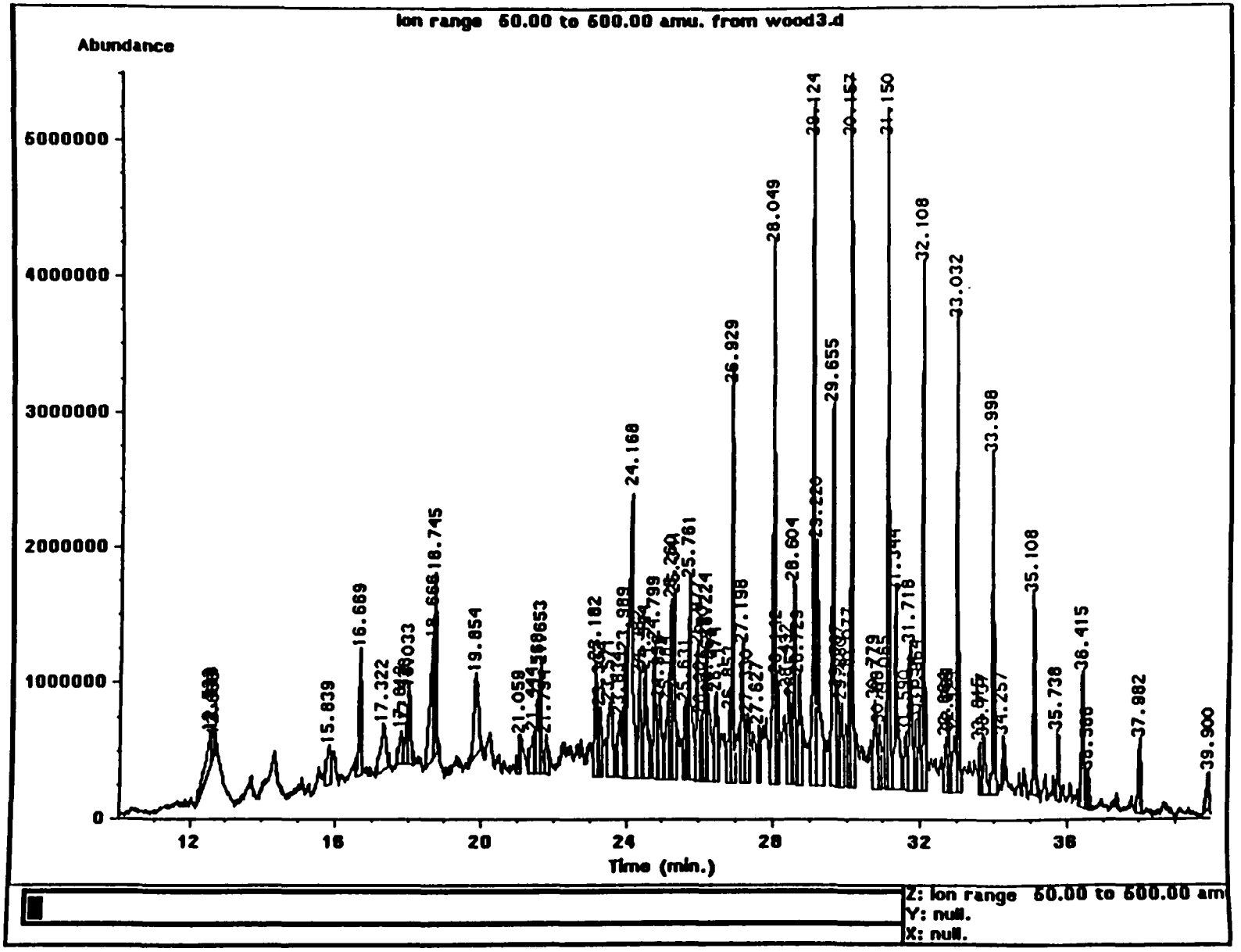


Figure 3-6. Mass spec chromatograph of Formica© board sample extracted from quartz fiber filter.

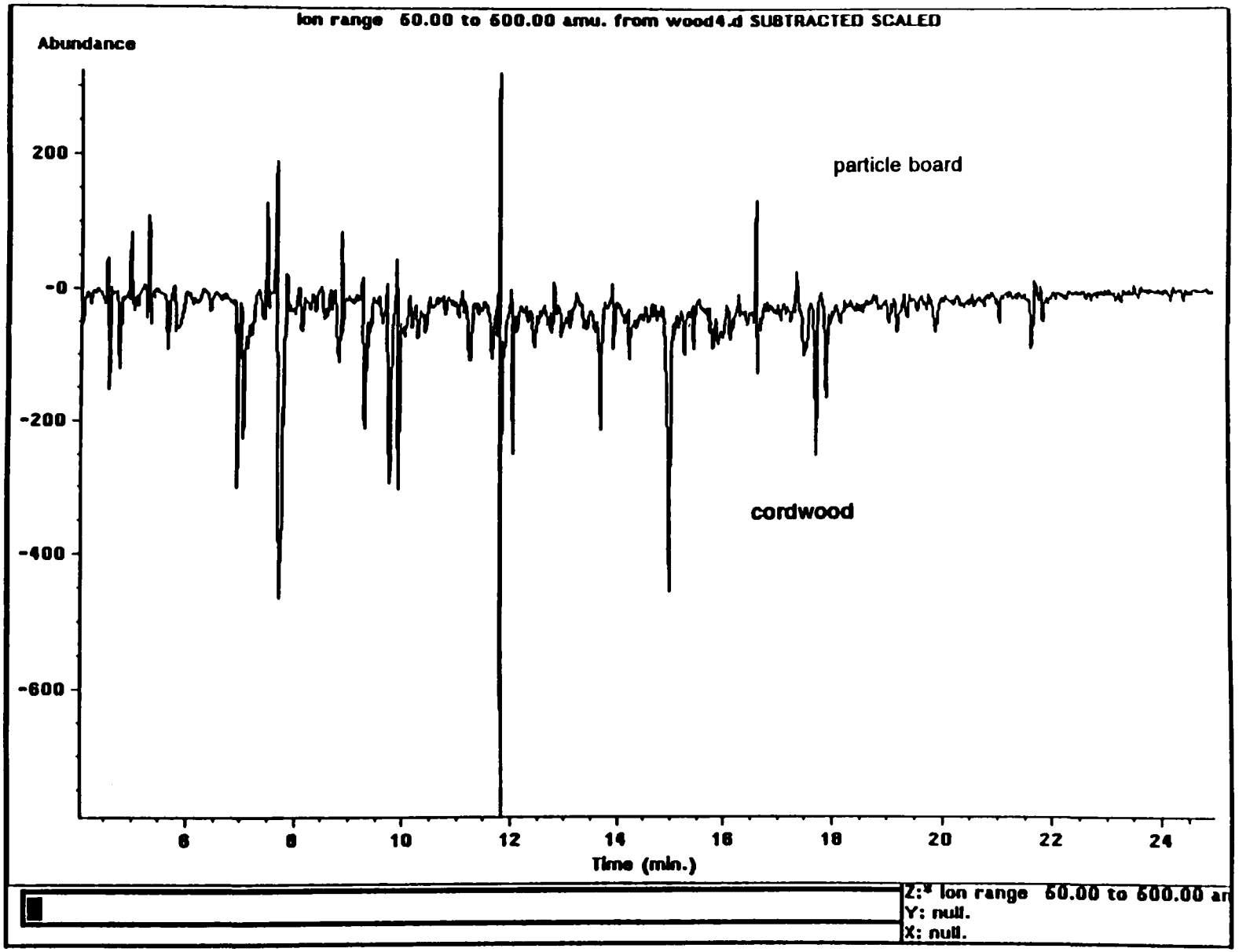


Figure 3-7. Mass spec chromatograph subtraction of cordwood sample from particle board (XAD-2 resin extract).

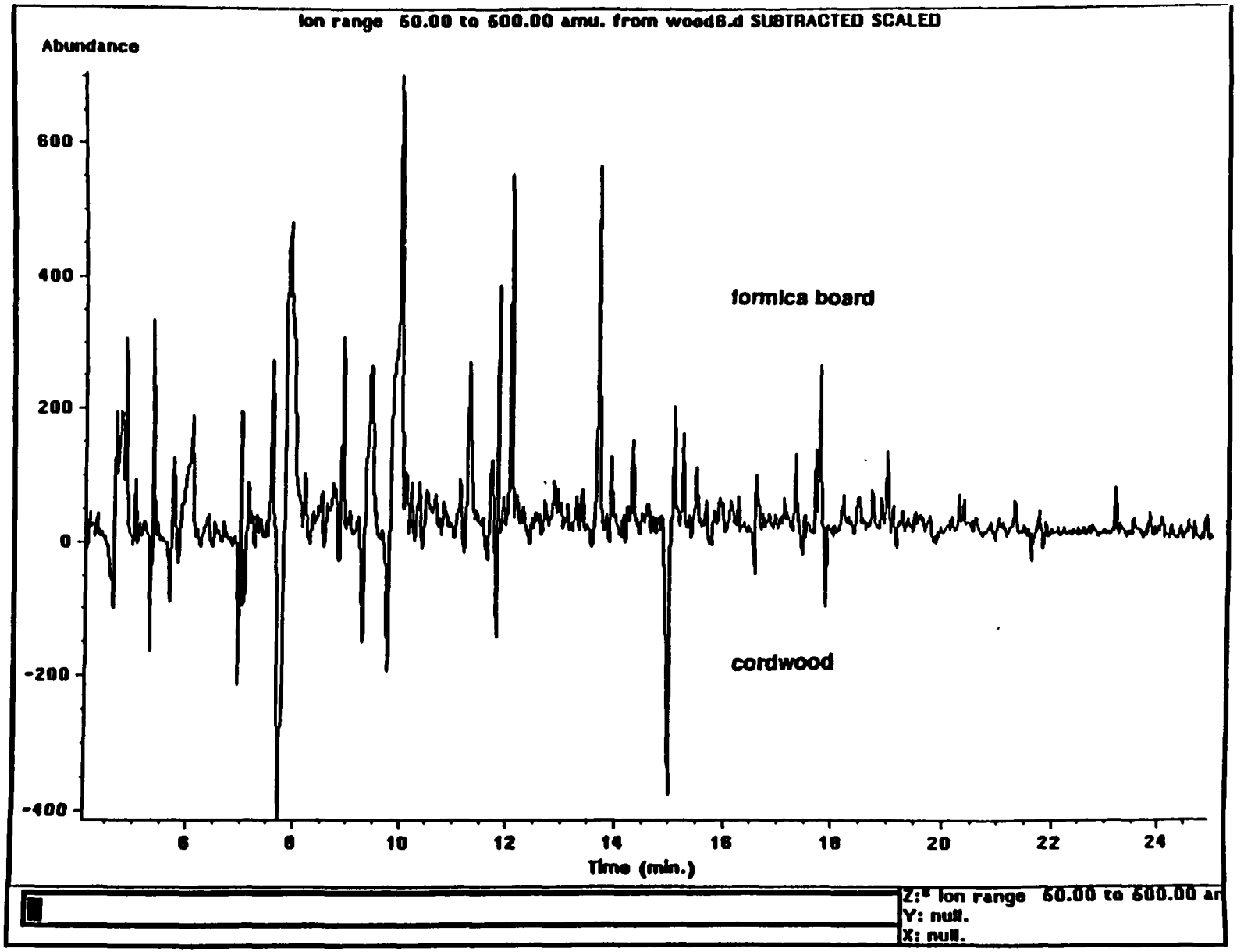


Figure 3-8. Mass spec chromatograph subtraction of cordwood sample from Formica© board (XAD-2 resin extract).

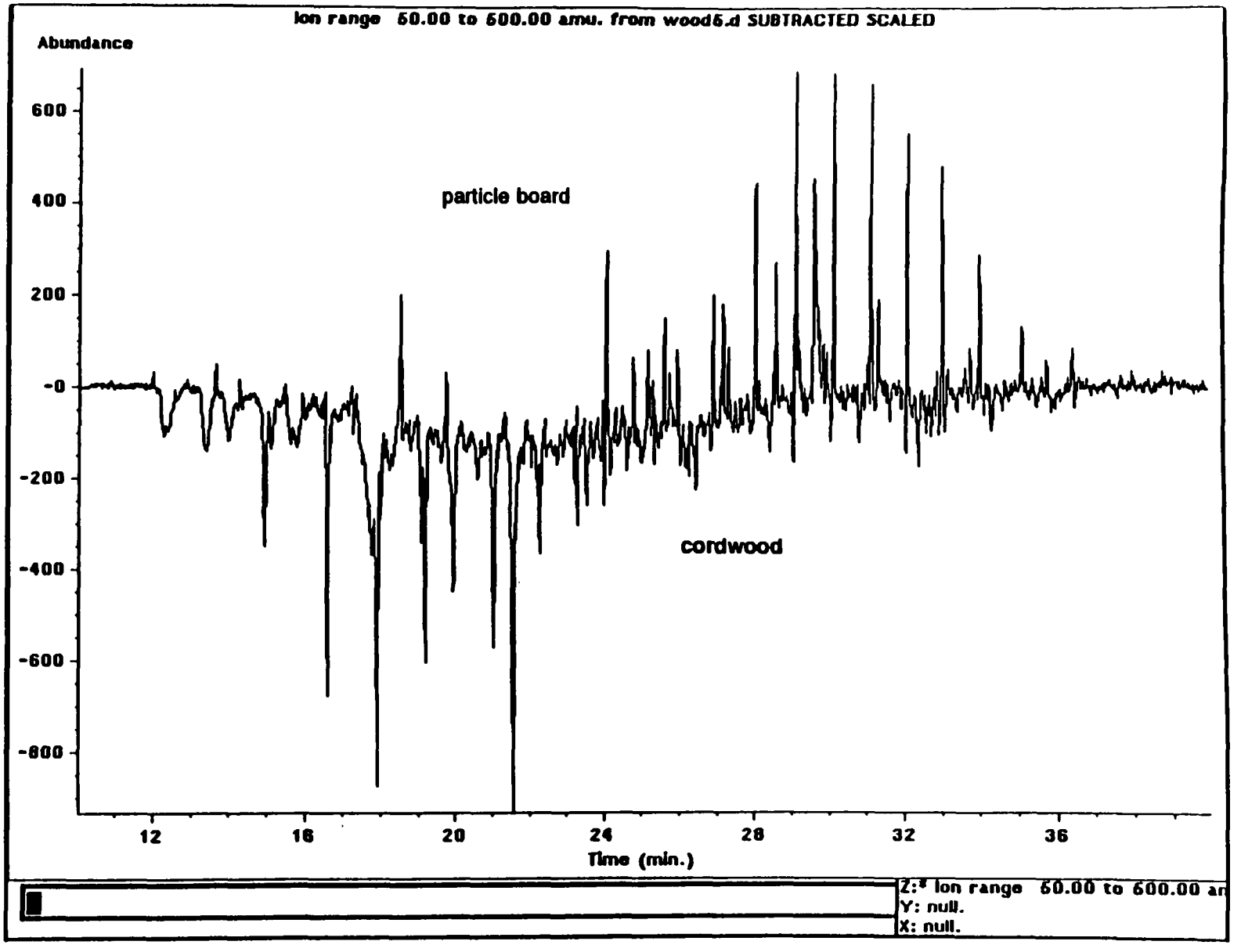


Figure 3-9. Mass spec chromatograph subtraction of cordwood sample from particle board (filter).

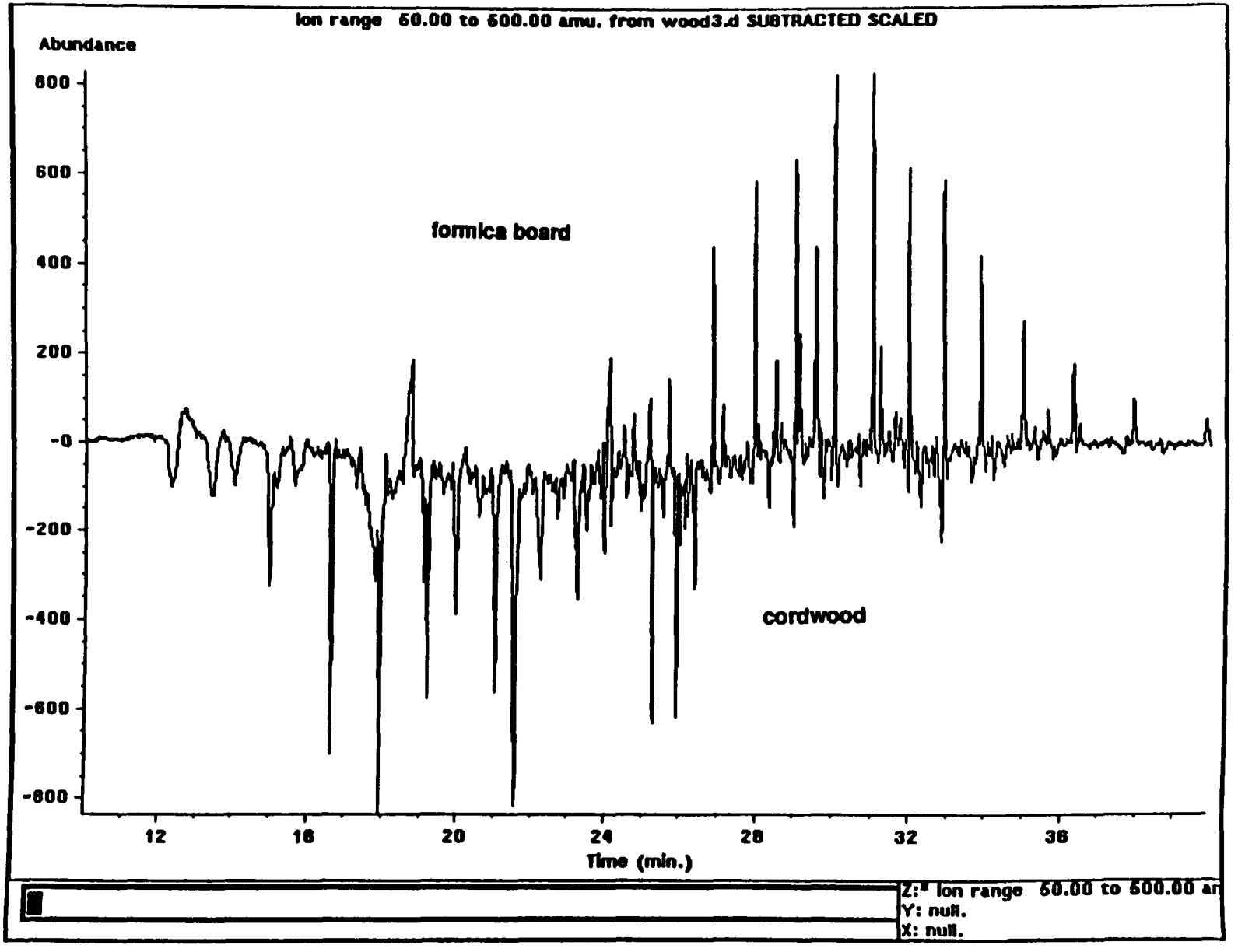


Figure 3-10. Mass spec chromatograph subtraction of cordwood sample from Formica© board (filter).

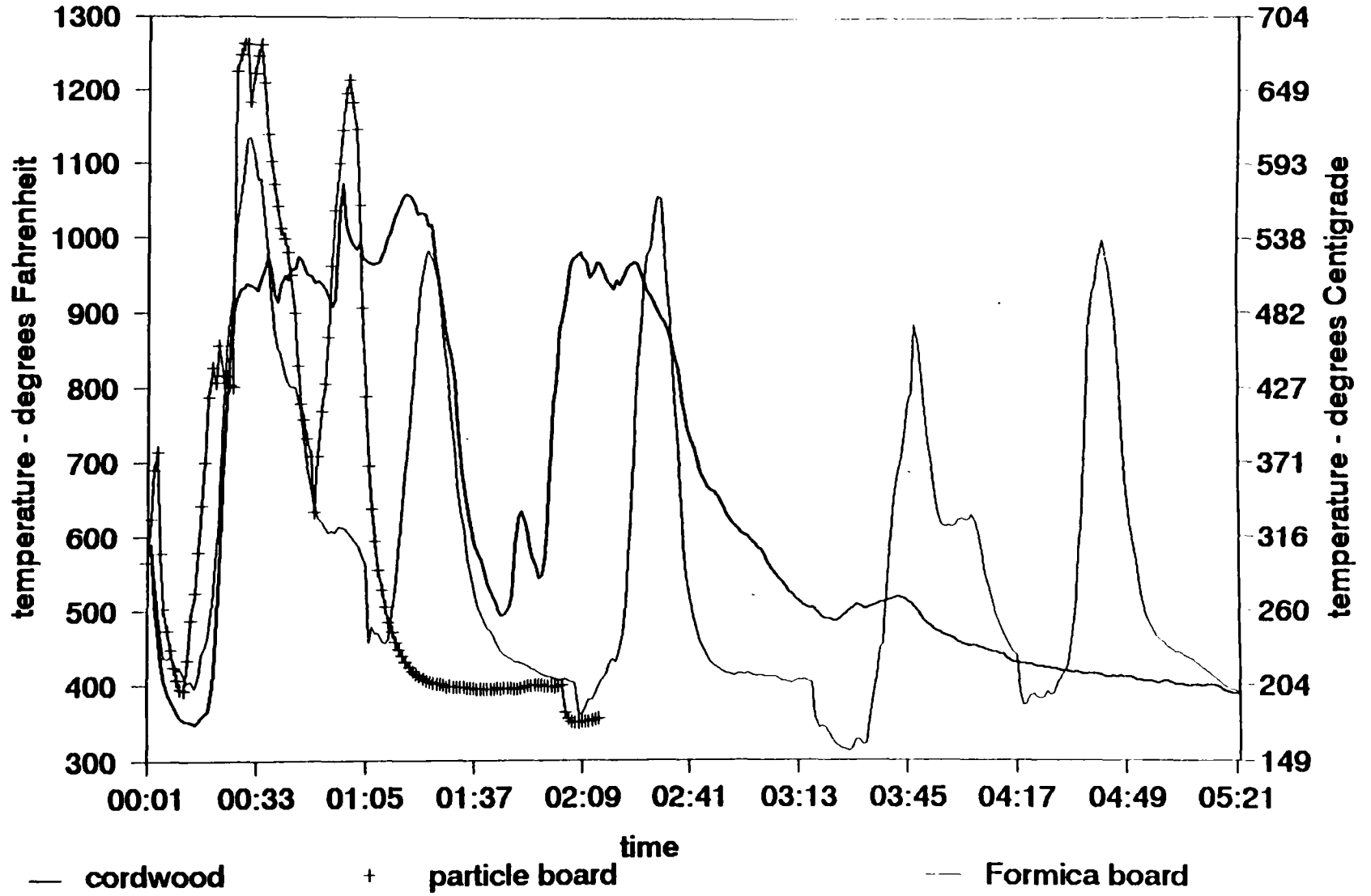


Figure 3-11. CEM temperature.

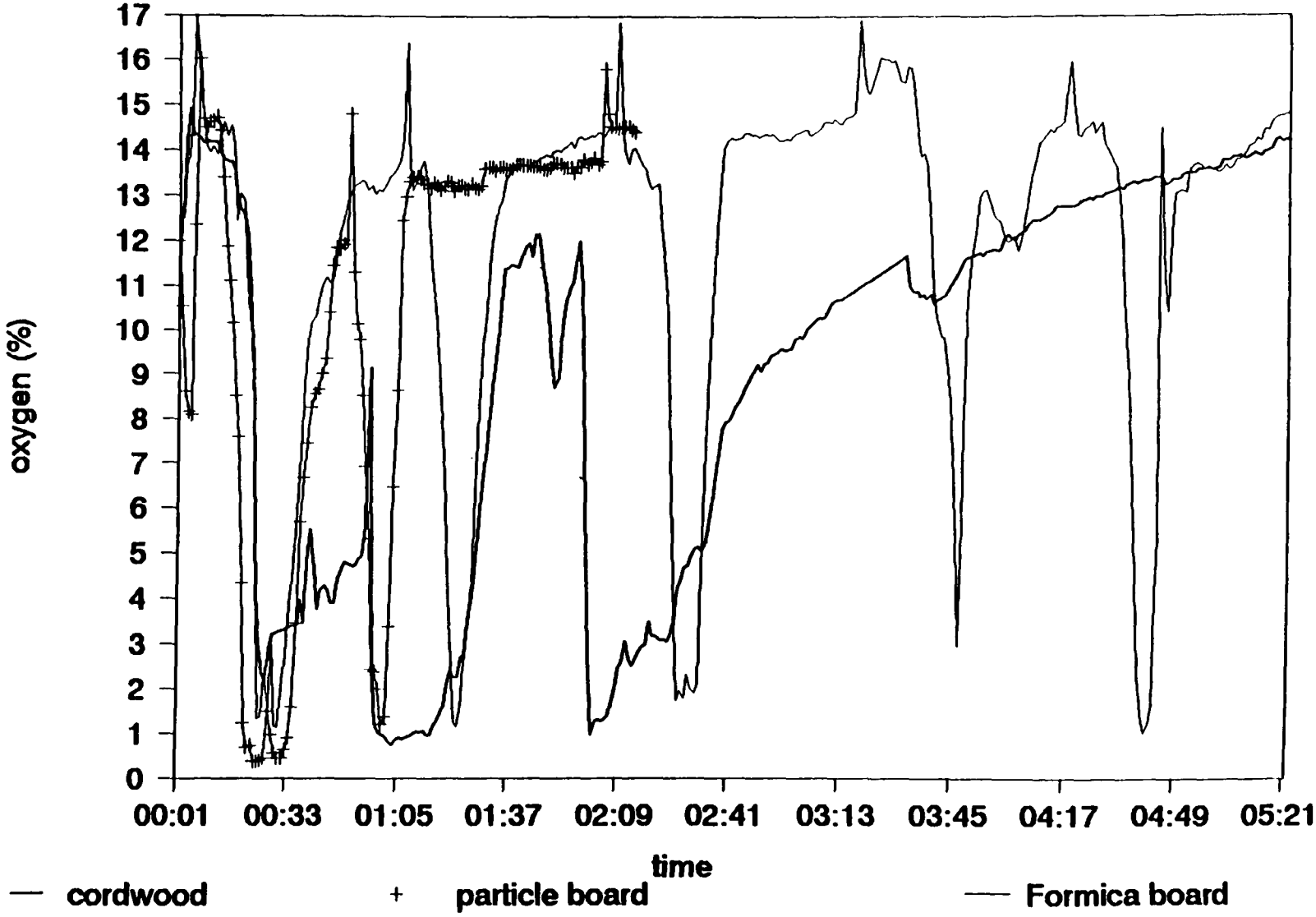


Figure 3-12. CEM O_2.

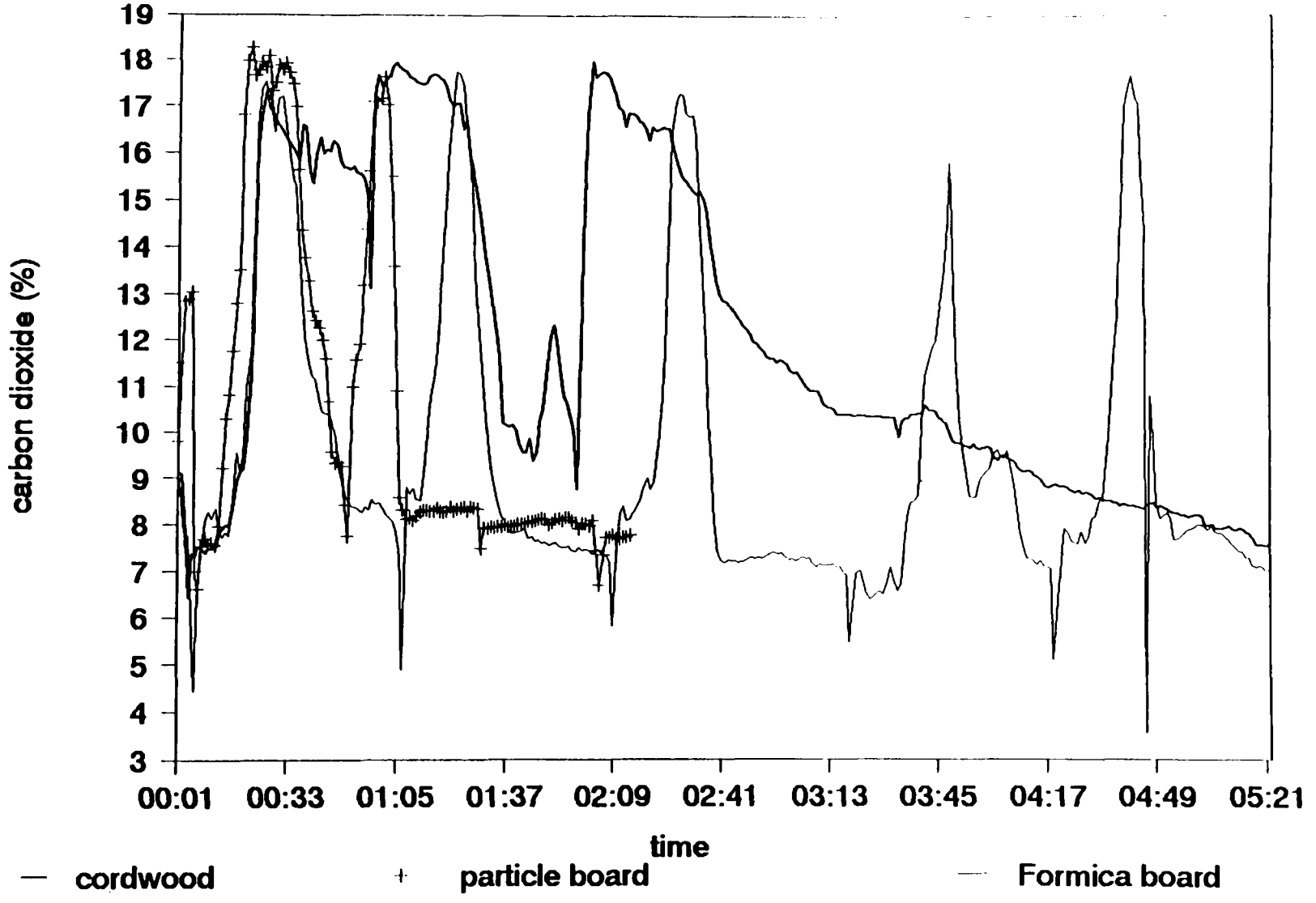


Figure 3-13. CEM CO_2.

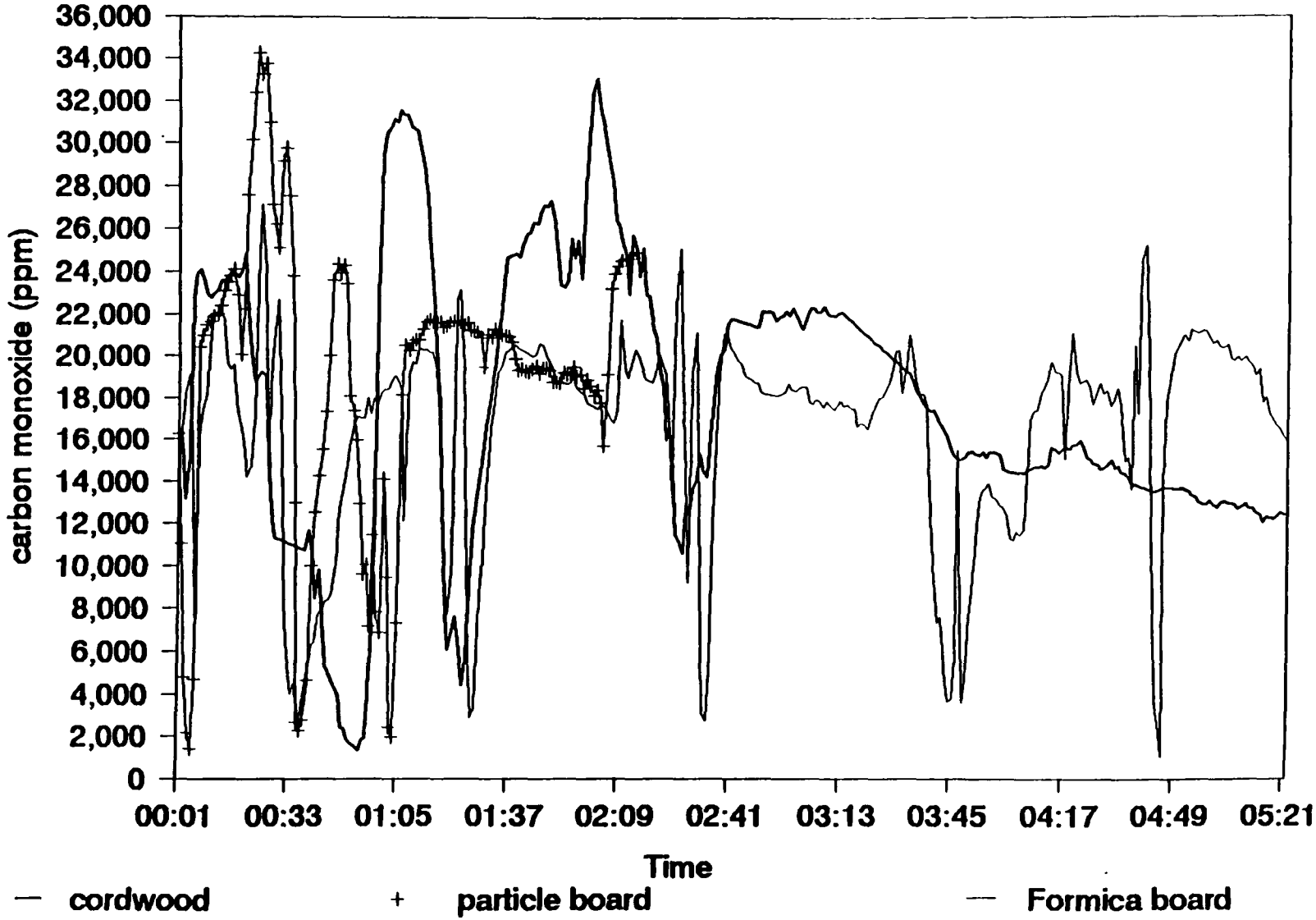


Figure 3-14. CEM CO.

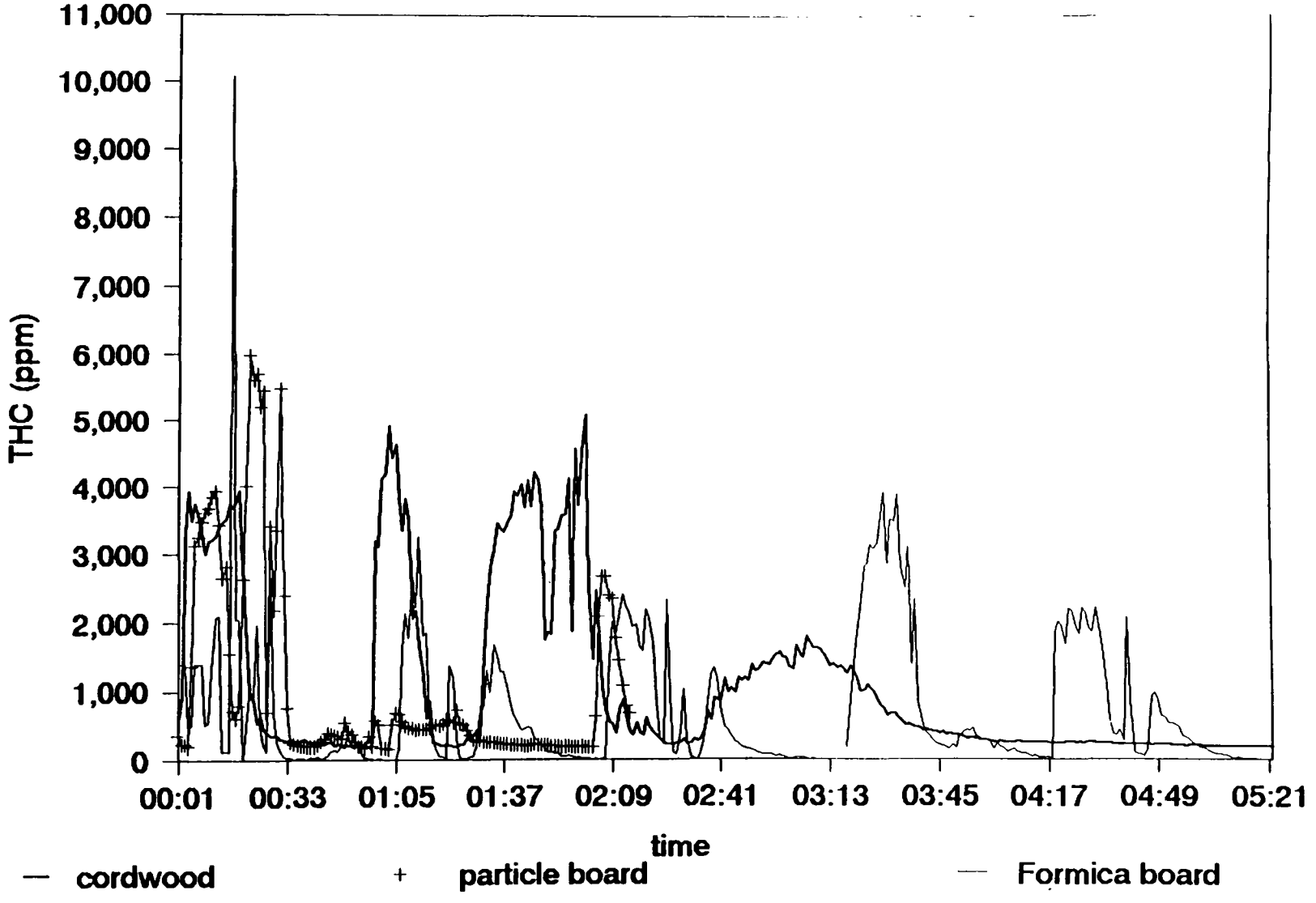


Figure 3-15. CEM total hydrocarbon (ppm).

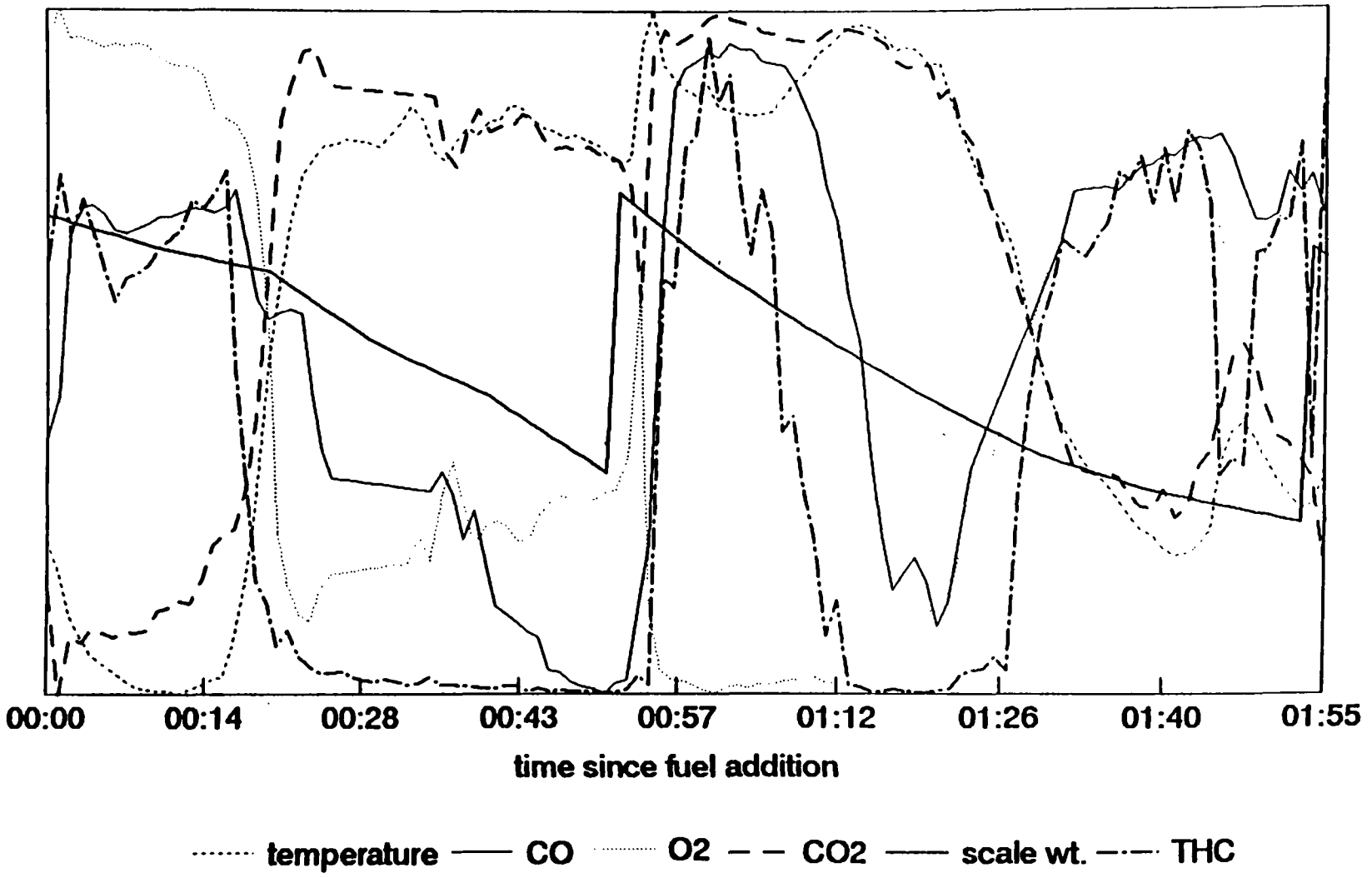


Figure 3-16. CEM data for cordwood burn (data normalized for comparison).

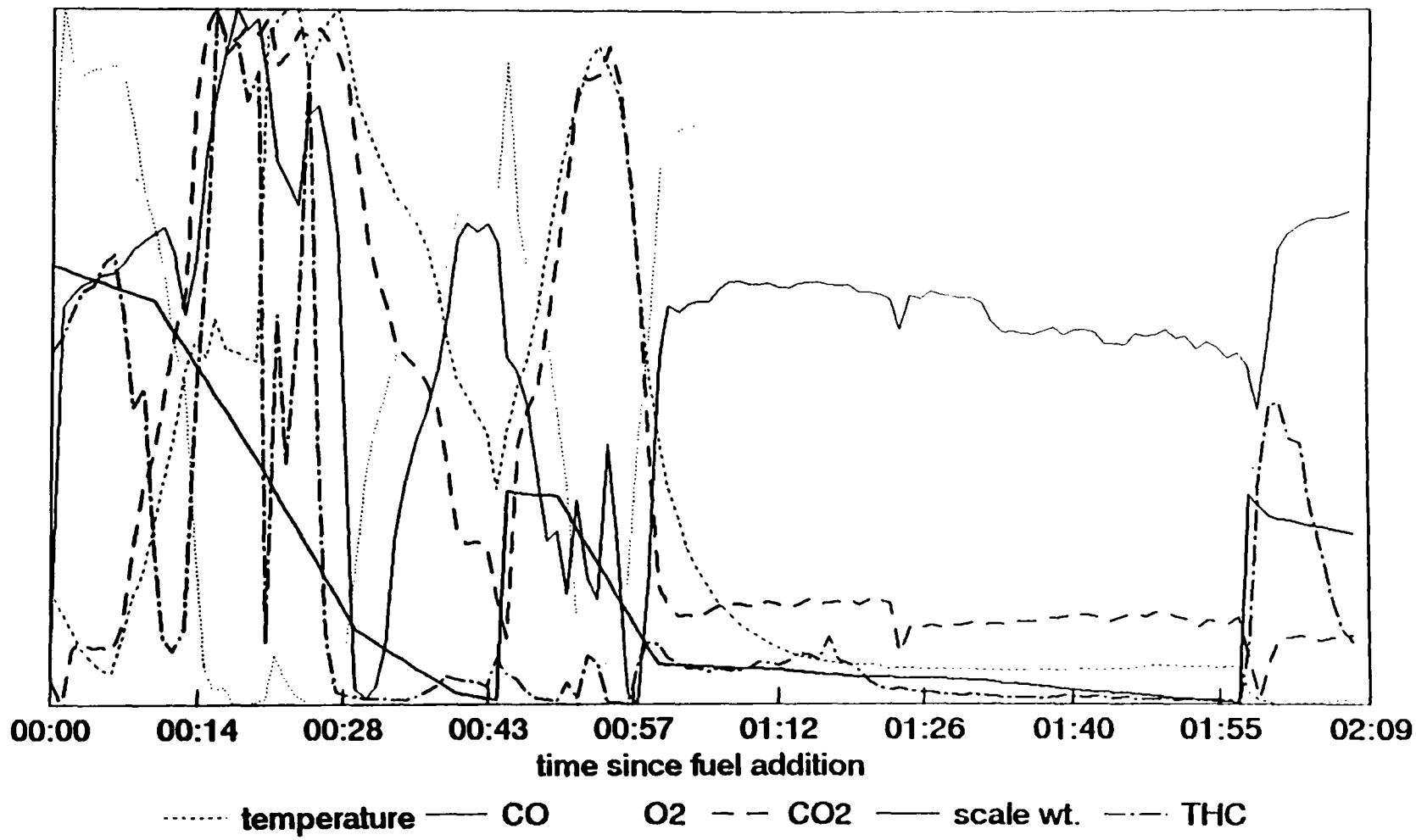


Figure 3-17. CEM data for particle wood burn (data normalized for comparison).

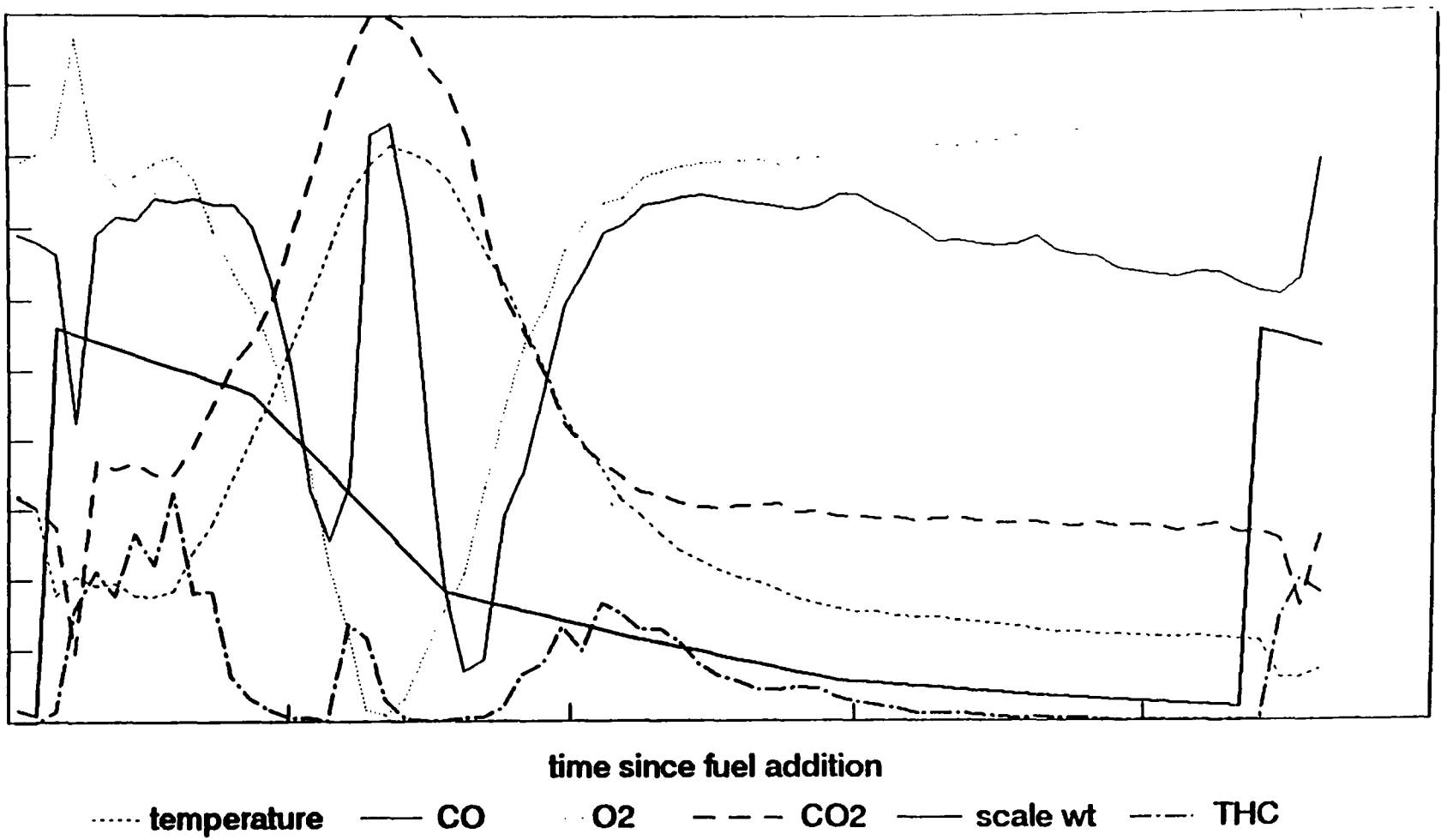


Figure 3-18. CEM data for Formica© burn (data normalized for comparison).

SECTION 4

DATA RESULTS AND DISCUSSION

Examination of the sampling data from Table 2-2 clearly shows that these sampling tests were not equivalent. During the October 10, 1992 particle board burn, high stack temperatures were observed when the previous day's cordwood settings were used. These stack temperatures were high enough that the diluted sample presented to the sampling media was well above ambient temperature. Attempts to control the burn rate with the inlet air were ineffective because of the cast grating draft control. The flue damper was then adjusted to provide greater dilution which successfully reduced the diluted stack temperature. Although Acurex Environmental could have modified the draft control to enhance its operation, the testing and modification of barrel stove kits was not the purpose of this project.

These high stack temperatures were the result of a higher burn rate. The composite woods (particle board and Formica© board), are burned as small scraps which provide a high surface area/mass of fuel. This ratio increases the volatilization of gaseous components to the combustion zone. Additionally, a large fraction of the composite wood consists of synthetic resins that are likely to have lower molecular weights and, by extension, higher vapor pressures than the wood components. These resins may also provide some of the oxygen necessary for combustion since they are manufactured from phenols and aldehydes.

Figure 3-11 compares the stack temperatures for the three fuels burned. It clearly shows the different nature of the composite wood combustion relative to cordwood. Manufactured wood combustion is characterized by higher maximum temperatures, sharp peaks, and deep valleys. Figures

3-12 through 3-15 show this same periodic nature during composite wood combustion for the other CEMs. Cordwood combustion CEM data, in contrast, show a more diffuse signature.

Figures 3-16 through 3-18 also present this different nature of the composite wood combustion by displaying the CEM data for the three fuels along with the scale data. The changes in slope for the scale data suggest that combustion occurs in multiple stages. The first stage is characterized by volatilization. Temperature and CO_2 levels remain low while hydrocarbons are emitted. CO tends to follow the total hydrocarbon trend. The second stage may be described as char combustion. At the beginning of this stage, the levels of hydrocarbons and CO go through a valley while CO_2 levels and temperature rise. As expected, oxygen is the inverse of CO_2. Apparently, a separate and distinct hydrocarbon emission is associated with each "stage" of the scale signal.

These relationships are present, to a lesser extent, in Figure 3-14 for the cordwood burn. The less distinct relationships are caused by overlap between fueling cycles when cordwood is burned. During the first cordwood fueling a distinct change of slope can be discerned in the scale data and the described relationships are visible. The second fueling occurs before the first has ended, meaning that the second volatilization stage overlaps the first char combustion. Even here, separate hydrocarbon emission phases may be observed, CO is related to hydrocarbon emission, and the stack temperature drops somewhat until hydrocarbon emission is finished.

Table 3-2 summarizes the emission data for the three burns. Clearly, the two composite woods produce less CO and total hydrocarbons than cordwood, but significantly greater amounts of the heavier compounds. This result is seen in the total capture and the VOCs (Because the Formica© board consists of particle board plus a laminate, its VOC emissions are likely to be similar) where the Formica© board total capture is twice the amount, and the particle board VOCs is nearly three times that of cordwood on a mass/mass basis. In terms of filter capture, NVOCs, and SVOCs, Formica© board has uniformly greater emissions than cordwood. Particle board, however, is actually closer to cordwood in these factors than it is to the Formica© board. In this study, particle board emitted the lowest SVOC levels.

As discussed earlier, the total capture includes the gravimetric analysis of the probe rinse, the filter capture, and the XAD-2 EOM. The reason why TCO analysis is not performed on the probe rinse is that, just as the probe rinse is a minor constituent of the total capture value, previous experience has shown that SVOCs are a minor constituent of the probe rinse sample which is to be expected as the probe rinse represents those materials which condense from the diluted sample stream. In other words, these components have boiling points greater than those which condense on the filter implying that most SVOCs, which collect initially on the probe, can be expected to return to the gas stream over the sampling period. Those remaining SVOCs are captured by occlusion in the heavier components. Additionally, the solvent used to prepare a probe rinse sample is acetone. The primary purpose of this operation is cleaning the probe. Methylene chloride has been shown to be incapable of completely removing the residues from the probe. The more polar acetone removes these residues more efficiently. Acetone is more reactive than methylene chloride and will modify some of the sample components. This sample modification is not particularly significant from a mass distribution point of view but would lead to questionable results when extract components are identified by GC/MS.

Aldehyde data are not reported because all results were below the detection limit of the analysis. It is not clear how to interpret these results. Several discussions were held regarding this analysis. All indications during sampling operations were that DNPH tube exposure proceeded normally. Sample flow through these tubes was recorded at 10-min intervals. These records have been reviewed, and no abnormalities were found. A distinct colored band was observed to form in the front tube and gradually move down over time. The sample tubes were refrigerated for the time between sampling and transfer to the analytical laboratory. Roy Zweidinger[3] has confirmed that refrigerated, derivatized aldehydes should remain stable over the time between sampling and analysis. No evidence that the samples were improperly collected or treated has been found.

Aldehydes were anticipated before this study was conducted based on the use of phenols and formaldehyde in manufacturing these resins and on previous studies which found aldehydes during the combustion of cordwood in air-tight woodstoves. The CEM data make it clear that combustion occurred

very differently in this barrel stove than in an air-tight stove. In a recent study of two non-catalytic woodstoves, for example, oxygen varied from 13-19 percent, CO_2 varied between 1-7 percent, and stack temperature ranged from 150-600 °F. These values are quite different from those reported in Table 3-1. A fireplace might provide a better comparison. We are not aware of any fireplace studies that included aldehyde results. However, based on this very limited data set, it cannot be concluded that aldehydes are not formed during wood combustion in a barrel stove.

VOC data were obtained only from the cordwood and particle board tests, the Formica© board sample was non-detectable. However, the total hydrocarbon data presented in Table 3-1 and Figure 3-15 for the Formica© burn suggest that this sample must have been bad, either during collection or handling before analysis. This VOC sample was inadvertently allowed to sit for a significant time before delivery to AREAL for analysis. In all likelihood, sample components reacted and condensed onto the container walls. Unfortunately, the limited funding of this study did not permit a repeat burn.

Table 3-3 presents these VOC results. In terms of relative concentrations compounds past benzene, certainly those past toluene, in retention time do not represent significant components of the sample. Benzene represents less than 0.5 percent of the cordwood sample and less than 0.1 percent of the particle wood sample.

The majority of the VOC mass was reported at the retention times of 10-15 min, which is the range containing 4-6 carbons. During this range, the column overloaded making integration of the peaks difficult. Thus all of the compounds within this range were reported as a few components. The overloading occurred for both samples. This range represents 97.8 percent of collected mass for the cordwood test and 99.8 percent for the particle board. The two samples had many of the same light molecular weight compounds, but the cordwood had more of the heavy compounds. The chromatograph contains many unidentified compounds. Those compounds were included in the table to reflect the quantity and types of compounds that may be found in that range. Some differences between the two can be attributed to the type of wood and to the binders used in the particle board.

The filter and XAD-2 extracts were analyzed by GC/MS to identify their components. Figures 3-1 through 3-6 represent the total ion chromatograms (TICs) from the analysis of these six samples. Figures 3-7 through 3-10 present the difference spectrum for the four composite wood samples minus the corresponding cordwood sample. Figures 3-9 and 3-10 are the most striking showing a strong trend to longer retention times for the filter samples from the composite woods. The fact that the GC column used for this work separates primarily on the basis of boiling point, suggests a trend towards higher molecular weight components for the composite woods. Tables 3-4 through 3-6 present the library search results for these GC/MS tests. Each table includes both the filter and XAD-2 sample for that wood. Table 3-7 presents the easiest comparison of the compounds generated from the three burns while Table 3-8 presents some observations by compound class.

1. Two compounds (2,4-hexadiene-1-ol and naphthalene) were observed for all three woods.
2. Five compounds (6,7,10,12, and 18) were not found in the particle board samples. However, this absence may be due more to the lower total fuel burned during the particle board burn than to any real differences in combustion chemistry.
3. The majority (21,25,26,29, and 31) of the polycyclic aromatic hydrocarbons (PAHs) are observed only in the cordwood samples.
4. None of the saturated hydrocarbons were observed in the cordwood sample. Nearly half of the compounds identified in the manufactured fuel samples were saturated hydrocarbons.
5. 4-Hydroxyl-benzenesulfonic acid is found in both the manufactured fuel samples while isocyano-benzene is found only in the Formica© board samples. The presence of this compound suggests the starting materials for Formica© laminate described in Hawley's dictionary.

GC/FID analysis and GC/MS analysis were performed with the same type of column and oven temperature program. Unfortunately, the GC/MS's vacuum changed those retention times enough to make peak matching between the two analyses extremely difficult.

Ash samples were analyzed by GC/FID (TCO) and gravimetric methodology. The mass collected from the ash samples was below the quantifiable limits of the GRAV method and the TCO detection limit.

SECTION 5

QUALITY ASSURANCE

Field and lab blanks were collected to establish background emission levels. Field and lab blanks were collected for XAD-2 cartridges and filters while only field blanks were collected for DNPH tubes. No blanks were collected for the probe or the VOC canisters because each canister is analyzed before sampling. Field blanks were delivered to the sampling site, opened, resealed, and returned to the lab. Lab blanks remained sealed until extraction. XAD-2 and filter emission results were blank corrected. Table 5-1 presents the percent of blank mass compared to the average of the actual sample mass.

Completeness for data recovery is described in Table 5-2. DNPH tubes yielded non-detectable samples. One VOC canister failed to yield a sample, but all other samples were intact. Conditions and observations recorded during and after sampling indicated that samples had been collected by these techniques. More than two months elapsed between sampling and analysis. Samples may have been lost or degraded during this period.

TABLE 5-1. PERCENT BLANK MASS OF AVERAGE SAMPLE MASS

% field blank of avg XAD-2 TCO	0.07
% field blank of avg XAD-2 GRAV	0.91
% field blank of avg filter TCO	4.17
% field blank of avg filter GRAV	1.46
% field blank of avg filter total capture	0.40

TABLE 5-2. COMPLETENESS OF DATA

	Data points	Completeness
CEMs	15	100%
Aldehydes	13	100%
VOC	3	67%
GRAV	8	100%
GC/FID	8	100%
GC/MS	6	100%
Filter capture	4	100%
Probe rinse	3	100%

CEMs were calibrated before and after each test using three different concentrations of span gas appropriate to each instrument.

The balance used for gravimetric analysis was sensitive to 10 µg/weighing, but any mass less than 6 mg/sample was determined as below quantifiable limits, and any mass less than 1.2 mg/sample was considered to be below detectable limits as follows:

- Detection limit = (10 µg)* (3)* (sample volume 10 mL)/(aliquot volume 0.25 mL) = 1.2 mg
- Quantifiable limit = detection limit (1.2 mg)* (5) = 6 mg

The GC/FID used for TCO analysis had a quantification limit of 0.014 µg and a detection limit of 0.003 µg. The quantification limit was set at the average mass of three hydrocarbons in our lowest concentration calibration standard. The detection limit was established at one-fifth the quantification limit.

SECTION 6

SUMMARY AND CONCLUSIONS

This study determined a number of differences between the combustion of composite woods and cordwood. These composite woods burn faster than cordwood because of the higher surface area of these composite woods, which are burned as scraps, relative to the same mass of cordwood. Higher stack temperatures and oxygen concentrations, and lower CO and total hydrocarbons (mass/mass basis) were observed during combustion of these composite woods versus cordwood.

VOC levels are much higher during the combustion of these composite woods with the major components being in the C_4-C_6 region. Total emission levels (based on the total capture value) are also higher for these composite woods. Higher total capture results such as these are due, in large part, to higher NVOC levels. SVOC levels, on the other hand, are equivalent (Formica©) or even lower (particle board) than those generated by cordwood. There is a trend toward larger molecular weight components for these emissions. The filter extracts for these composite woods show higher concentrations of higher retention time analytes during the GC/MS analysis. These components were primarily straight chain hydrocarbons.

Significant differences were observed in the compounds identified from the extractable organics. A majority of the PAHs are associated with the cordwood rather than the composite wood combustion. Additionally, isocyano-benzene was identified from the Formica© samples and 4-hydroxyl-benzenesulfonic acid was found in the composite wood samples.

No aldehydes were detected from any of the samples collected during this study. The meaning of this information is not clear. Based on air-tight woodstove studies, aldehydes were expected from at

least the cordwood samples. However, the combustion conditions during this study are probably closer to those of a fireplace than a woodstove. No significance can be attached to these aldehyde results without further testing.

SECTION 7

REFERENCES

1. Sax, N.I., and Lewis, R.J., Hawley's Condensed Chemical Dictionary 11th ed.; Van Nostrand Rinehold Company, Inc., New York, 1987.

2. Lentzen, D.E., Wagoner, D.E., Estes, E.D. and Gutknecht, W.F. (1978) IERL-RTP Procedures Manual; Level 1 Environmental Assessment 2nd ed.; EPA-600/7-78-201 (NTIS PB 293795).

3. Personal communication from R. Zweidinger, USEPA/AREAL, to M. Tufts, Acurex Environmental, Oct. 1, 1992

APPENDIX A

RELATED RECOMMENDED OPERATING PROCEDURES

INTERIM PROCEDURE

This procedure has been authorized for reference as an interim procedure by the AEERL QAO. The procedure will undergo extensive EPA review prior to finalization.

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RECOMMENDED OPERATING PROCEDURE FOR GRAVIMETRIC ANALYSIS OF ORGANIC EXTRACTS

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RECOMMENDED OPERATING PROCEDURE FOR GRAVIMETRIC ANALYSIS OF ORGANIC EXTRACTS

1.0 PROCEDURAL ELEMENTS

1.1 Scope and Application

Organic compounds with boiling points of 300°C and higher, after extraction with methylene chloride, evaporation of the solvent, and drying to constant weight, can be determined quantitatively by the gravimetric analysis described in this procedure.[1] This method is applicable to organic liquids, solid sample extracts, aqueous extracts, and extracts from the Source Assessment Sampling System or Modified Method 5 train sorbent module. This analysis should be performed after enough of the sample extract has been concentrated to weigh accurately.[2] The suggested solvent is methylene chloride because of its good extraction properties and high volatility. Other solvents may give different results (e.g., methyl alconol may extract polar compounds which would not be extracted with methylene chloride). All samples being dried to constant weight should be stored in a desiccator.

The range of applicability is limited by the sensitivity of the balance and the organic content of the sample. The balance must be accurate to $\pm$ 0.01 mg. If a sample of five milliliters is used for the analysis, then a sensitivity of 0.01 mg/5 mL or 0.002 mg/mL of sample can be achieved. This can be improved by further concentration of more sample.

1.2 Definitions

- o Method Blank: Provides a check on contamination resulting from sample preparation and measurement activities. Typically run in the laboratory after receipt of samples from the field by preparing a material known not to contain the target parameter. Addresses all chemicals and reagents used in a method.

- o Reagent Blank: Provides information on contamination due to specific chemical reagents used during sample preparation, plus any background from the measurement system.

- o Audit Sample: Has known "true values," but is flagged for the laboratory as a "performance evaluation (PE) sample." Provides information on performance, but this information must be tempered with the understanding that the sample may be given extra attention by the analyst. An internal PE sample is created by the in-house analytical laboratory, while an external PE sample is created outside of the analytical laboratory.

1.3 Interferences

Results may be biased due to contamination of the solvent, glassware, or both. A method blank (control) shall be run in duplicate for each run lot of solvent and/or set of samples to provide a control check on the purity of the solvent and the glassware cleaning procedure. The method blank, consisting of a solvent sample from the same lot as that used to prepare samples, shall be prepared and concentrated in an identical manner.

Two reagent blanks shall be analyzed each day samples are run to ensure results which are not biased due to solvent contamination. The reagent blank shall be a solvent sample from the same lot used to prepare the samples and shall not be concentrated prior to analysis. To minimize error in weight due to moisture condensa-

tion, the pans containing the sample must appear visually dry before being placed in a desiccator in preparation for drying to constant weight.

1.4 Apparatus

(1) Analytical Balance: Capable of weighing 0.01 mg with an accuracy of ± 0.005 mg.

(2) Desiccating Cabinet: Seal-tight door gasketed with gum rubber. (Desiccators which use silicone sealant shall not be used because of possible contamination of the sample. Silicone grease may interfere with subsequent analysis.)

(3) Oven: Capable of operation to 175°C.

(4) Fume Hood: Standard laboratory.

(5) Dust Cover, Plexiglas, or equivalent: To protect samples drying in hood.

1.5 Reagents and Materials

(1) Disposable Aluminum Weighing Pans: Approximately 2" in diameter, 1/2" deep; crimped sides; weighing approximately 1.0 grams.

(2) Tweezers.

(3) Aluminum Foil.

(4) Pipets: 1 to 5 mL (Class A Volumetric).

(5) Glass Beakers: 50 to 400 mL.

(6) Wash Bottles, Teflon or equivalent.

(7) Deionized Water.

(8) Nitric Acid/Sulfuric Acid, 50:50 (V/V): Prepared from reagent-grade acids.

(9) Methylene Chloride: Burdick and Jackson or equivalent grade.

(10) Methyl Alcohol: Burdick and Jackson or equivalent grade.

(11) Drierite and/or Silica Gel: New Drierite or silica gel may be used as received. Used Drierite or silica gel may be reactivated by drying it in an oven for at least two hours at 175°C.

1.6 Sample Handling

All apparatus that contacts either the concentrated or evaporated residue samples shall be glass, Teflon, aluminum, or stainless steel. Evaporation of samples shall be carried out in an area free of airborne dust and organic vapors that could contaminate the samples.

Ordinarily, all glassware coming in contact with a sample, in either dilute or concentrated form, must be cleaned by complete Level 1 procedures.[2] Briefly, this entails sequential cleaning with soapy water, deionized water, 50:50 (V/V) nitric acid/ sulfuric acid, deionized water, methyl alcohol, and methylene chloride, followed by oven drying. The use of deionized water for cleaning glassware is critical when inorganic substances are being analyzed or heavy metal contaminants are present in high concentration in tap water.

This ROP, however, covers only the analysis of organic constituents. Tap water can be substituted for deionized water in glassware cleaning whenever the organic concentration exceeds one mg/sample as measured by this ROP. Experience has shown that tap water adds no measureable amount of organic contaminants to the method or reagent blanks under these conditions.

1.7 Sampling/Analysis Procedures

(1) Label aluminum sample pans on the underside using a ballpoint pen or other sharp object. Handle dishes only with clean tweezers.

(2) Clean the weighing pans by first rinsing them with deionized water, then dipping them successively into three beakers of methyl alcohol, methylene chloride, and, finally, methyl alcohol again.

(3) Dry the cleaned weighing pans to constant weight on a shelf lined with clean aluminum foil in an oven heated to at least 105°C. Cool the pans in a desiccator for a minimum of 4 to 8 hours or overnight.

(4) Weigh pans to constant weight to an accuracy of ± 0.01 mg, recording the pan tare weight.

(5) Transfer by pipet a 1.0 mL aliquot of the sample to the aluminum sample pan or use 1/10 of the concentrated sample. Aliquot size must never exceed 5 mL to avoid loss of sample through capillary action.

(6) Place the sample pan on a clean piece of aluminum foil in a clean fume hood. Shield the pan from dust with a Plexiglas or other cover positioned to allow for adequate air circulation. Evaporate sample to visual dryness at room temperature. This usually takes about 30 minutes.

(7) Place sample pan in desiccator over Drierite and/or silica gel for at least 8 hours.

(8) Weigh sample pan at approximately 4-hour intervals until three successive values differ by no more than ± 0.03 mg. If the residue weight is less than 0.1 mg, concentrate more sample in the same sample pan. If there is insufficient sample remaining for this purpose, report the initial value obtained, along with an explanation.

1.8 Calculations

The gravimetric range organics (GRAV) is calculated in units of mg/sample as follows:

$$GRAV = \frac{(\text{Sample Weight}_{mg} + \text{Pan Weight}_{mg}) - (\text{Pan Tare Weight}_{mg})}{\text{Aliquot Volume}_{ml}/\text{Total Concentration Sample Volume}_{ml}}$$

The calculated GRAV weight is corrected for the method blank:

$$\overline{\text{GRAV CORRECTED}} = \text{GRAV MEASURED} - \text{METHOD BLANK}$$

1.9 Data Reporting

The results of the analysis are averaged and reported in units of mg organics/original sample.

1.10 Precision

Duplicate analyses shall be run by the same analyst and shall be rejected if results differ by more than 20% from the average. If insufficient material is present to rerun the sample, both values will be reported with a qualifying statement.

1.11 Accuracy

Dry sample weight should be at least 1 mg per analysis whenever possible. Accuracy of the analysis is $\pm$ 20% of actual value. A proficiency test should be performed by each analyst as described in Section 2.0

2.0 QUALITY CONTROL ELEMENTS

- All operators should demonstrate proficiency with Gravimetric Analysis of Organic Extracts (GRAV) prior to sample analysis. In the proficiency testing, include a GRAV analysis of a reagent blank, a method blank, and an audit sample. The method or reagent blank shall be less than 5 mg/mL of sample. Results of the audit sample shall be within the precision and accuracy specifications outlined in this ROP.

- Two types of audit samples are used. The first contains 100 mg of eicosane [$CH_3(CH_2)_{18}CH_3$] in 250 mL of methylene chloride. Concentrate this solution to 10 mL in a manner identical to that used for sample preparation prior to GRAV analysis. The second type of audit sample can be either prepared in-house or received from an independent laboratory. It must contain organic compounds with chain lengths of more than 18 carbons (and boiling points above 300°C) in sufficient concentration to be determined accurately. Perform the GRAV analysis in duplicate as described in Section 1.7 of this procedure.

- Determine the GRAV value of duplicate method blanks for each new lot of solvent and/or set of samples. Run a method blank any time contamination is suspected. Prepare the blank using the same lot of reagent and the same concentration procedure as that used to prepare the samples. The solvent sample shall be an equivalent volume to that used for sample preparation. If the blank GRAV value is unusually high (i.e., 5 mg/mL of sample), find the cause of the contamination and repeat the method blank GRAV analysis.

- Analyze two reagent blanks for GRAV each day samples are run to ensure the results are not biased due to solvent contamination. The reagent blank shall consist of an aliquot of the solvent used to prepare the samples. If both reagent blank GRAV values are high (i.e., 2 mg/mL of sample), find the cause of the contamination and reanalyze samples and reagent blanks.

- Analyze all samples in duplicate. Samples are analyzed by the same analyst and must agree to within 20% of the average. In the event this condition is not met, repeat the analyses.

  NOTE: If the conditions require the sample to be reanalyzed (e.g., high blank values or poor precision) and insufficent sample remains, then report the value obtained by the initial analysis and include a qualifying statement.

3.0 REFERENCES

1. Harris, J.C. et al. Laboratory Evaluation Level 1 Organic Analysis Procedure. EPA-600/S7-82-048, NTIS PB 82-239, pp. 30-36, March 1982.

2. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. IERL Procedures Manual: Level 1 Environmental Assessment (Second Edition). EPA-600/7-78-201, NTIS PB 293-795, pp. 26-142, October 1978.

INTERIM PROCEDURE

This procedure has been authorized for reference as an interim procedure by the AEERL QAO. The procedure will undergo extensive EPA review prior to finalization.

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RECOMMENDED OPERATING PROCEDURE FOR TOTAL CHROMATOGRAPHABLE ORGANICS (TCO) ANALYSIS

by

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Disclaimer: This recommended operating procedure has been prepared for the sole use of the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

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RECOMMENDED OPERATING PROCEDURE FOR TOTAL CHROMATOGRAPHABLE ORGANICS (TCO) ANALYSIS

1.0 PROCEDURAL ELEMENTS

1.1 Scope and Application

This method provides semi-quantitative data for organic compounds with boiling points between 100°C and 300°C. Samples that might include organic compounds in this volatility range are organic liquids, solid sample extracts, aqueous extracts, extracts from Source Assessment Sampling System (SASS) and Modified Method 5 (MM5) train sorbent modules, and liquid chromatography (LC) fractions obtained from those samples. This method is based on separating the components of a gas or liquid mixture in a gas chromatography (GC) column and measuring the separated components with a suitable detector.

The upper end of applicability is limited by column overloading and detector saturation. Typical range is 1 to 20 mg/mL. The operating range can be extended by dilution of samples with solvent (e.g., dichloromethane). The sensitivity limit shall be determined by the minimum detectable concentration of standards.

1.2 Summary of Method

TCO analysis quantifies chromatographable material with boiling points in the range of 100° to 300°C. This analysis is applied to all samples that might contain compounds in this volatility and boiling point range.

For TCO analysis, a 0.9- to 3-uL portion of the extract is analyzed by gas chromatography using a flame ionization detector (F.I.D.). Column conditions are described in this document in tabular form in section 1.5.

The peak areas are converted to concentration values using quantitative calibration standards.

For more information, consult Lentzen et al., IERL Procedures Manual: Level 1 (reference 1).

1.3 Definitions

- QC Sample:
  This sample is prepared from a stock solution in an identical manner as the calibration standard. Its concentration is approximately midway in the linear working range of the GC. This quality control (QC) sample is run daily along with the sample set.

- Method Blank:
  Also called concentrated solvent blank, the method blank provides a check on contamination resulting from sample preparation activities. It is typically prepared in the laboratory alongside a sample set by "extracting" and concentrating the appropriate amount of clean solvent in the desired size extraction apparatus.

1.4 Interferences

The analytical system shall be demonstrated to be free from internal contaminants on a daily basis by running a bakeout or a QC sample. A reagent blank must be run for each new batch of reagents used to determine that reagents are contaminant-free. This is verified by an instrument response less than the detection limit.

If duplicate runs of a sample show increasing concentration greater than 15%, or if cross-contamination is suspected (e.g., high-level sample followed by a low-level sample), a reagent blank shall be run to verify no contamination in the system. If contamination is evident, the column shall be baked out at approximately 250°C for 20 minutes or until the detector is stable, and the blank check repeated.

1.5 Personnel Requirements

This ROP is written for individuals with a BS/BA degree in chemistry and at least two years experience in gas chromatography, or equivalent.

1.6 Facilities Requirements

This procedure requires a standard analytical chemistry laboratory with counter space, secured areas for compressed gas storage, and electricity to operate the equipment. Flasks, beakers, tubing, etc. customarily found in such a laboratory are also needed and assumed to be readily available. GC tools (e.g., wrenches, screwdrivers, spare parts, etc.) need to also be available in the laboratory.

1.7 Safety Requirements

Routine safety precautions required in any analytical chemistry laboratory are applicable here. These include such measures as no smoking while in the laboratory; wearing safety glasses, lab coats, and gloves when handling samples; handling organic solvents in a fume hood, etc. Compressed gases considered to be fuels (e.g., hydrogen) must be stored on a pad outside the confines of the laboratory. A safety shower, eye wash, first aid kit, and fire extinguisher must be readily available inside the laboratory.

1.8 Apparatus

1. Gas Chromatograph - GC with packed column and/or capillary column capabilities, oven temperature controller, and flame ionization detector (F.I.D.). (e.g., Perkin Elmer Sigma 115 or Hewlett Packard 5890.)

2. Autosampler - (optional) - Capable of handling methylene chloride extracts and appropriate wash vials.

3. Autosampler vials (optional) - Clear glass vials with teflon faced crimp caps, typically 100 microliter or 1 mL size.

4. Crimping Tool (optional) - Used to secure caps on autosampler vials.

INSTRUMENTAL OPERATING CONDTIONS FOR GAS CHROMATOGRAPHY

Column	Temperature Program (optional)	Injector	Detector	Carrier Gas	Split Injector (optional)	Injection Volume	Solvent
Fused Silica Capillary Column (15 meters typically DB-1, DB-5, or equivalent)	40°C for 3 minutes 8°C/min increase to 250° C and hold for total run time of 45 minutes	300°C	F.I.D. 300°C	Helium 1-3 mL/min	10/1 split ratio	Not to exceed 3 ul (Typically 1 ul)	Dichloromethane (pesticide grade, distilled in glass or equivalent)
Packed Column (Methyl Silicone oil coated at 10% on Supelcort AW DMCS or equivalent 1/8 in. x 6 ft. steel)	50°C for 5 minutes 20°C/min increase to 250°C, then hold	300°C	F.I.D. 300°C	Helium at 30 mL/min	N/A	1-5 ul	Dichloromethane (pesticide grade, distilled in glass or equivalent)

N/A = Not Applicable

1.9 Reagents and Materials

1. Methylene Chloride: Burdick and Jackson or equivalent grade.

2. Syringe - 5 or 10 microliter, gas tight, syringe for hand injections. Otherwise, 3 or 10 microliter syringes are used for autosampler injections.

3. Disposable Pasteur Pipets - Used for sample transfer.

4. Pipet bulbs - 1 mL, amber.

5. Teflon Squeeze Bottle - 250 mL, or equivalent, used for methylene chloride rinse of vials.

1.10 Samples/Sampling Procedures

NOTE: All glassware coming in contact with a sample shall be cleaned by Level 1 procedures (ref. 1). Briefly, this entails sequential cleaning with soapy water, deionized water, 50:50 (V/V) nitric acid/sulfuric acid, deionized water, methyl alcohol, and methylene chloride, followed by oven drying.

1.10.1 Sampling/Analysis Procedures

(1) Start up by the manufacturer's suggested method.

*(2) Replace septum on auto-sampler and column.

*(3) Insure injection needle is in line with injection port. The autosampler needle should be manually "injected" through the injection port to verify alignment.

(4) Bakeout GC at 200°C for 20 minutes until F.I.D. response is stable and all evidence of column contamination is gone (no peaks) or run an injection of clean solvent as the first injection of the day to verify column contamination is eliminated.

*(5) Load auto-sampler tray with samples.

*(5A) Check the autosampler flush by placing the autosampler in manual mode and flushing a vial of clean solvent through the needle assembly.

*(6) Set auto-sampler to inject approximately 1 uL of samples. Capillary column can be damaged if too great a volume is injected.

(7) Run a QC standard using the specified conditions to verify that the system is operating properly. Check the TCO window (C_7 - C_{17} to insure the range has not changed. (Retention times may change with column aging.) The TCO window for calculations should be adjusted as required.

(8) Flush needle with solvent (dichoromethane) between injections.

(9) Run samples and collect data.

(10) Analyze data according to prescribed method.

(11) After all analyses are complete, bakeout the column at 200°C for 20 minutes, or run clean solvent as a "sample."

(12) Shut down instrument by method suggested by manufacturer.

* These steps are only applicable to automatic injection.

1.10.2 Preparation

Samples for TCO analysis arrive or are prepared as methylene chloride (or occasionally as methanol) extracts of environmental samples, filters, resins, or ambient sampling components. An aliquot of the extract is transferred to a TCO vial and loaded into the autosampler as required.

1.11 Sample Stability

All samples will be stored in a refrigerator at or below 4°C to retard analyte degradation. Samples will be analyzed as soon as possible after sample receipt and preparation to avoid loss of sample due to volatilization and degradation.

1.12 Calibration

(1) Preparation/dilution of a stock solution: Weigh approximately 100 uL aliquots of each (heptane, decane, dodecane, tetradecane, and heptadecane, C7, C10, C12, C14, C17) (99% + pure) into a 10 mL volumetric flask or septum-sealed vial. Quantitative calibration of the TCO procedure is accomplished by the use of mixtures of known concentration of the normal hydrocarbons decane, dodecane, and tetradecane. Retention time limits correspond to the TCO range of boiling points and are defined by the peak maxima for n-heptane (C7, B.P. 98°C) and n-heptadecane (C17, B.P. 303°C). Therefore, integration of detector response should begin at the retention time of C7 and terminate at the retention time of C17. The C7 and C17 peaks are not included in this integration. By this procedure, the integrated area will cover material in the boiling range of approximately 100°C to 300°C. Weigh each hydrocarbon successively into the vial starting from least volatile to most volatile.

(2) Dilute the vial contents up to approximately 3 mL with dichloromethane.

(3) Transfer this quantitatively to a clean, 10-mL amber volumetric flask and add dichloromethane up to the 10-mL mark. This stock solution will have approximately 22 mg (C7 to C12)/mL and 15 mg (C14 to C17)/mL. Several (at least three) dilutions of the stock solution are made to cover the linear working range.

1.13 Sample Analysis

A portion of the extract is injected into the GC under the conditions specified. The peak area (F.I.D. response/uL) is summed over the TCO range window and corresponding TCO value (mg/mL) is determined from the calibration curve. In the event that the TCU value is outside the linear working range, the sample shall be concentrated or diluted, depending on the requirement, and re-analyzed. If there is not enough sample to concentrate, the values are reported as found, and an appropriate qualifying statement is included in the analytical report.

It is important that the observed values of the total integrated area for samples be corrected by subtracting an appropriate solvent blank, prepared in the same manner as the samples.

1.14 Calculations

The peak area (F.I.D. response/uL) is summed over the TCO window and a corresponding TCO value (mg/mL) is determined from the calibration curve.

(1) Construct the calibration line by fitting a linear regression equation to the results of the analysis of the calibration standard solution. The concentration of the standards must fall within the linear working range of the instrument and bracket the concentration of the sample. Use the C10 to C14 standards for calibration.

Standard Calibration Equation:

$$R_i = (M)\ C_i + (B)$$

R_i = F.I.D. Response (total C10 to C14 Peaks)
C_i = Concentration mg/L (total of C10 to C14 standards)
M = Slope of line
B = Intercept of line

(2) Calculate the TCO value for the sample (C_U, measured value) and blank (C_B, blank value) by summing the F.I.D. response over the TCO retention time span and calculating the concentration from the calibration equation.

It is important that the observed values of the total integrated area for samples be corrected by subtracting an appropriate solvent blank prepared in the same manner as the samples. The sample is corrected for the blank:

$$C_U \text{ corrected} = C_U \text{ measured} - C_B$$

1.15 Data Reporting

The results of each TCO analysis should be reported as one number (in milligrams), corresponding to the quantity of material in the 100°C to 300° boiling range in the original sample collected. If more information is available (e.g., cubic meters of gas sampled), the mg/sample value can then be easily converted to the required reporting units.

1.16 Corrective Action

Corrective action procedures in this ROP are covered in the QC check (2.1) and QC control (2.2) sections of the document.

1.17 Precision

Duplicate results by the same operator will be rejected if they differ by more than 15%.

1.18 Accuracy

The result of a quality control sample, run daily, will be considered deficient if it differs by more than 15% from the preparation value. If this value falls outside the accepted range, the system must be evaluated for the probable cause and a second standard run or a new calibration performed over the range of interest.

2.0 QUALITY ASSURANCE/QUALITY CONTROL

2.1 QC Checks

- All glassware used in the TCO analysis shall be cleaned by the method described in reference 1.
- Change the GC inlet septum daily; follow this with a column bakeout at 300°C for twenty minutes or until the F.I.D. response is stable and all evidence of contamination is gone (no peaks) or run an injection of clean solvent to verify column contamination is eliminated. Repeat this procedure during the run if evidence of septum failure appears (e.g., increasing peak elution time with each run or major loss of sensitivity).

2.2 QC Controls

- Run a reagent sample for each new batch of reagent or lot of solvent used. If the analysis fails to show organic contaminants to be below detection limits under identical instrument operating conditions as used for samples, then the reagent shall be distilled in glass and retested or the reagent batch will be unacceptable for TCO analyses.

- Calibrate the GC with standards that generate a response/concentration curve. The calibration curve must be 1 and must have a correlation coefficient greater than 0.97 to b acceptable.

- Prepare a QC standard that is approximatey mid-way in the linear working range. Run this QC standard daily to verify the performance of the GC. Determine the TCO value using the calibration curve and its value plotted compared to the theoretical value. If two runs of the QC standard differ by more than 15% of the actual value, prepare a new QC standard and repeat the test. If the new sample fails the test, determine if there is a loose column connection, septum, or altered split flow. After correction, run a new QC standard. If the new sample fails the test, recalibrate the instrument and/or perform a column change if needed.

3.0 REFERENCES

1. Lentzen, D. E., D. E. Wagoner, E. D. Estes, and W. F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition). EPA 600/7-78/201, NTIS No. PB293-795, pp. 140-142, October 1978.

INTERIM PROCEDURE

This procedure has been authorized for reference as an interim procedure by the AEERL QAO. The procedure will undergo extensive EPA review prior to finalization.

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STANDARD OPERATING PROCEDURE FOR EXTRACTION OF FILTERS AND SOLIDS

by

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Prepared for

The AEERL TECHNICAL SUPPORT OFFICE

Disclaimer: This standard operating procedure has been prepared for the sole use of the Air and Energy Engineering Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

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STANDARD OPERATING PROCEDURE FOR EXTRACTION OF FILTERS AND SOLIDS

1.0 PROCEDURAL ELEMENTS

1.1 SCOPE AND APPLICATION

Gaseous emissions sampling devices use a wide variety of filter papers and solids as substrates to entrap particulates. Filter papers are frequently made of Teflon, glass, or quartz; solids may be standard reference materials, sands, dusts, ashes, etc. Organic material adsorbed on particulates collected by these filters and solids is efficiently extracted before concentration and subsequent analysis.

Methylene chloride, because of its good extraction properties and high volatility, is the solvent of choice. The extraction is performed in an appropriately sized Soxhlet extractor. This standard operating procedure (SOP) may be used if the filter or solid substrate will fit into a Soxhlet extraction thimble and if the organic compounds adsorbed on the particulates are soluble in methylene chloride.

1.2 SUMMARY OF METHOD

Organic material that is adsorbed on particulates entrapped on filters and solids used in gaseous emissions sampling is extracted with methylene chloride in a Soxhlet extractor. The extract is then concentrated to an appropriate volume for subsequent organic analysis.

1.3 DEFINITIONS

- Method Blank: Provides a check on contamination resulting from laboratory sample preparation activities. Typically run in the laboratory after receipt of samples from the field. Addresses all chemicals, reagents, and apparatus used in a method.

1.4 INTERFERENCES

Possible contamination from an unused "clean" filter or solid, solvent, or glassware can be determined by running a method blank (see sections 1.3 and 2.0).

1.5 PERSONNEL REQUIREMENTS

This SOP is written for individuals with at least a year of organic chemistry and preferably also a year of experience in an organic research laboratory.

1.6 FACILITIES REQUIREMENTS

This procedure requires a standard wet organic chemistry laboratory with balances, a fume hood, electricity, water, refrigerator or freezer for sample storage, and a 110°C drying oven. The beakers, flasks, ring stands, clamps, tubing, etc. customarily found in such a laboratory are also needed and are assumed to be readily available.

1.7 SAFETY REQUIREMENTS

Routine safety precautions needed in any organic laboratory are applicable here. These include such measures as no smoking in the laboratory; wearing safety glasses, lab coats, and rubber gloves; handling organic solvents in a fume hood, etc. A safety shower, eye wash, first aid kit, and fire extinguisher must be immediately available in the laboratory.

1.8 APPARATUS

NOTE: Size of apparatus depends on size of filter or quantity of solid being extracted.

1. Soxhlet Extractor Assembly: Flask with appropriately sized extraction tube, thimble, and condenser.

2. Heating Mantle: Sized for Soxhlet flask.

3. Rheostat.

4. Boiling Chips, Teflon.

5. Snyder Column, 3-Ball.

6. Concentrator Tubes, Kuderna-Danish.

7. Frit, Sintered Glass.

1.9 REAGENTS AND MATERIALS

1. Methylene Chloride: Burdick and Jackson or equivalent grade.

2. Water, Deionized.

3. Glass Wool. Clean by sequential immersion in three portions of methylene chloride. Dry in a 100°C oven. Store in a methylene chloride-rinsed glass beaker covered with aluminum foil.

4. Aluminum Foil.

5. Pasteur Pipette, Glass, Disposable.

6. Flask, Volumetric: 10 or 25 mL.

7. Storage Vials, Brown or Clear, with Teflon-lined Screw Caps.

1.10 SAMPLES/SAMPLING PROCEDURES

NOTE: All glassware coming in contact with a sample shall be cleaned by Level 1 procedures.[1] Briefly, this entails sequential cleaning with soapy water, deionized water, 50:50 (V/V) nitric acid/sulfuric acid, deionized water, methyl alcohol, and methylene chloride, followed by oven drying.

1.10.1 Preparation

Samples for extraction arrive as particulates adsorbed on filters or on solids. The substrate filters and solids must have been weighed prior to use in the field if the weight of particulates is to be determined

in this SOP. (This is not always the case.) Remove the sample from its container and prepare it for insertion into a Soxhlet extraction thimble, using either (1) or (2) as described below:

(1) Fold filters coated with particulates into a cone with the point down and particulates facing inward, then place on tared aluminum foil. Fold the aluminum foil over the folded filter to prevent loss of particulates. Weigh. Record tare and final weights.

OR

(2) Transfer solids with entrapped particulates to an appropriately sized tared container. Weigh. Record tare and final weights.

1.10.2 Extraction

1. Perform this extraction using an appropriately sized Soxhlet extractor assembly. Solid samples of 30 grams or less and single filters of Teflon, glass, or quartz up to 8" X 10" can be extracted in a 500 mL apparatus. Solid samples weighing between 30 and 200 grams and multiple filters require a 3-liter (Size G) apparatus.

2. Use an all-glass extraction thimble with a coarse frit recessed 5-15 mm above a crenulated ring at the thimble bottom to facilitate drainage.

3. Cover the frit with a plug of cleaned glass wool to prevent particulates from clogging the pores.

4. Load the thimble with the sample prepared as described in section 1.10.1.

5. Place a plug of cleaned glass wool on top of the sample to prevent particulates from floating on top of the methylene chloride solvent used for extraction.

6. Assemble the Soxhlet extractor apparatus. Fill the round-bottomed flask two-thirds full with methylene chloride. Place the flask on a heating mantle with temperature controlled by a rheostat. Place thimble containing the sample into the extractor tube and attach tube to flask. Attach condenser to top of extractor tube. Start the flow of cooling water through condenser jacket.

7. Turn on the Soxhlet and extract with methylene chloride for 24 hours.

8. Turn off the Soxhlet. Remove the condenser. Depending on the size of the apparatus, rinse the extraction tube and thimble with 10 to 50 mL of methylene chloride. Collect and combine all rinsings in the Soxhlet flask.

9. In a clean fume hood, place the flask containing the methylene chloride extract and rinsings on a heating mantle with temperature controlled by a rheostat. Add Teflon boiling chips to the flask, if necessary, to prevent bumping.

10. Attach a 3-ball Snyder column pre-wetted with methylene chloride to the flask. To prevent any foreign material from entering the flask, fit the top of the column with a ground glass adapter attached to a bent glass tube. Direct the open end of the tube towards the rear of the hood.

11. Concentrate the extract to the appropriate volume by maintaining a temperature just high enough to boil off the methylene chloride.

12. Use methylene chloride to quantitatively transfer the concentrate to Kuderna-Danish tubes for further concentration, if necessary. Attach the same 3-ball Snyder column used in step 10 to the Kuderna-Danish tube and concentrate to the appropriate volume. Remove any contaminating particulates by filtering the concentrate through a sintered glass frit into a small flask.

13. Rinse the Snyder column with small portions of methylene chloride. Collect and combine all rinsings. Combine rinsings with the concentrate from step 12.

14. Using a Pasteur pipette, transfer the sample quantitatively to a volumetric flask and dilute to the mark with methylene chloride. (A 10 mL or 25 mL flask is the size used most frequently.)

1.10.3 Storage

Store the sample in either a Teflon-taped volumetric flask or a brown or clear vial with a Teflon-lined screw cap. Place in a refrigerator or freezer.

1.11 CALIBRATION/STANDARDIZATION

Calibration and standardization are not applicable to this SOP which covers only extraction and not analytical procedures.

1.12 ANALYSIS PROCEDURES

This extraction SOP does not stand alone, but is used in conjunction with numerous other SOPs which describe analysis procedures. Consult an appropriate analytical SOP (e.g., AEERL/12, Standard Operating Procedure for the Gravimetric Analysis of Organic Extracts) for analytical details.

1.13 CALCULATIONS

Let $P = particulates_{(mg)}$

$W_2 = (particulates + substrate + tare)_{(mg)}$

$W_1 = substrate_{(mg)}$

$T = tare_{(mg)}$

Then $P = W_2 - W_1 - T$

1.14 DATA REPORTING

The results are reported in units of mg particulates/sample.

1.15 CORRECTIVE ACTION

This SOP does not stand alone, but is used as a forerunner to numerous analytical SOPs. Consult the appropriate analytical SOP for corrective action procedures.

1.16 METHOD PRECISION/ACCURACY

This SOP does not stand alone, but is used as a forerunner to numerous analytical SOPs. Consult the appropriate analytical SOP for precision and accuracy requirements.

2.0 QUALITY CONTROL ELEMENTS

1. Determine a method blank by performing an extraction using the same size of Soxnlet apparatus and the same amount of glass wool, methylene chloride, and, if possible, unused "clean" filter or solid as employed in the extraction of the field sample. This method blank provides a check on contamination resulting from all sample preparation activities in the laboratory.

2. Perform a method blank along with each set of samples run. Any method blank value will eventually be subtracted from the sample value found in subsequent organic analysis.

3.0 REFERENCES

1. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht, "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA 600/7-78-201, NTIS No. PB-293-795, pp. 26, 136-142, October 1978.

RECOMMENDED OPERATING PROCEDURE FOR LARGE-SCALE XAD-2 RESIN PURIFICATION

by

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STANDARD OPERATING PROCEDURE FOR LARGE-SCALE XAD-2 RESIN PURIFICATION

1.0 PROCEDURAL ELEMENTS

1.1 Scope and Application

This recommended operating procedure (ROP) has been developed as an alternative to the small-scale XAD-2 resin purification procedure described in AEERL/25. It describes the purification of large amounts of XAD-2 resin for subsequent use in gaseous emission sampling. Commercial XAD-2 resin is impregnated with a bicarbonate solution to inhibit microbial growth during storage. The bicarbonate solution, any residual extractable monomer or polymer, and other residual organic material are removed by a series of aqueous and organic extractions. This ROP differs form AEERL/25 in that a chromatographic elution rather than a Soxhlet extraction is performed.

This ROP can also be employed to recycle resin used in field sampling, provided the resin has not been permanently discolored. Experience has shown that badly discolored resin cannot be purified well enough to pass the quality control checks described later in Section 2.1. Purification of recycled XAD-2 resin can begin at Step 4 of Section 1.8. The prior aqueous washings have been shown to be unnecessary to recycle the resin. This procedure should be used on an "as needed" basis. The purified resin should not be stored more than three weeks before use.

This procedure may not produce material suitable for ultra-trace level sampling and analysis since the allowable contaminated level is 1.75 mg/175 gram cartridge.

1.2 Summary of Method

This method is a chromatographable elution. Bicarbonate is first removed by soaking the resin in water. The wet resin is slurry transferred to an extraction tube and organic contaminants are eluted by sequentially pumping methanol, methylene chloride, methanol, and methylene chloride through the resin bed. The resin is ready for use in sampling after it has been dried under nitrogen and passed the quality control tests.

1.3 Personnel Requirements

This procedure requires one chemist or technician trained on this ROP.

1.4 Facilities

This procedure requires a laboratory set up for organic sample analysis. This laboratory should include a fume hood, a source of de-ionized water, solvent storage, glassware, and cleaning facilities. Because flammable solvents are used, the laboratory should be free of sources of flames or sparks when this purification procedure is performed.

1.5 Safety Precautions

This procedure uses flammable and halogenated organic solvents. There are known hazards of fire and of poisoning due to ingestion. There may also be hazards due to long-term exposure to methylene chloride fumes. There are no known hazards due to contact with XAD-2 resin. This procedure should be performed in a well-ventilated, no-smoking area. Sources of sparks or flames should be removed from the area. Personnel protection should include safety glasses, lab coats, and disposable gloves. Atmospheric monitoring for methylene chloride should also be considered.

1.6 Apparatus

(1) Extraction apparatus: see Figure 1

(2) Garbage pails, plastic, 25-gallon capacity

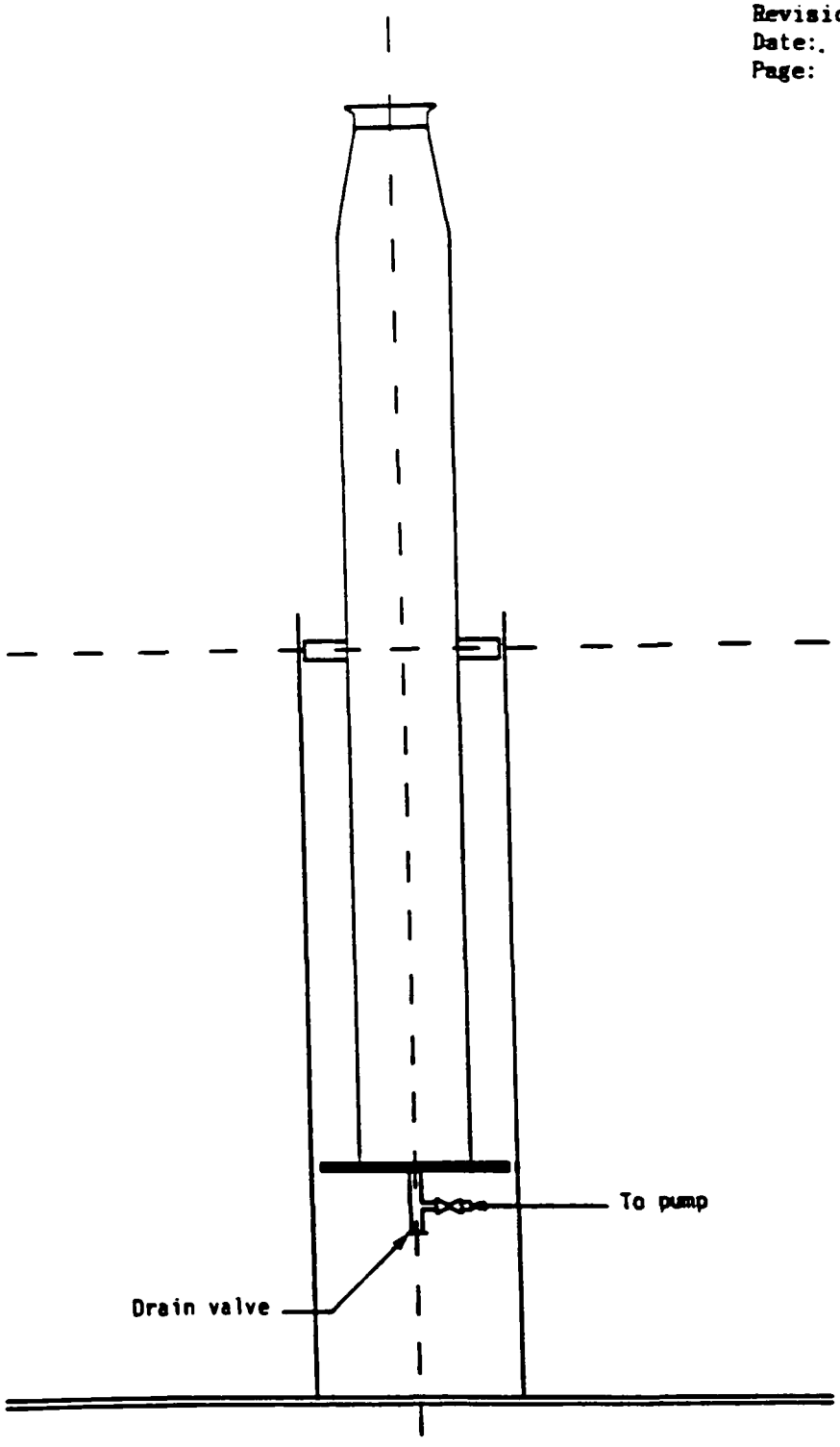

Figure 1. Cleanup Apparatus

(Dimensions withheld pending patent or publication)

(3) Autotransformer, variable: "Variac"

(4) Heat exchanger coil: see Figure 2

(5) Pump, variable speed: Teflon and stainless steel construction, capable of 0-3L/hr flow rate

(6) Dessicator, with rubber gasket

(7) Analytical balance: 0.01 mg resolution

(8) Gas chromatograph: with flame ionization detector

(9) Snyder Column, 3-ball

(10) Flask, Round-bottomed, 500 mL

(11) Flask, Round-bottomed, 500 mL

(12) Flask, Volumetric, 10 mL

1.7 Reagents and Materials

(1) Amberlite XAD-2 Resin: as supplied by Rohm & Haas, Co., Philadelphia, Pennsylvania; 7.5 kg

(2) Water, Deionized

(3) Methanol: Burdick and Jackson or equivalent grade

(4) Methylene Chloride: Burdick and Jackson or equivalent grade

(5) Nitrogen, Liquified: low pressure tank, National Welders, Airco, or equivalent grade

(6) Storage Bottles, Solvent: brown, gallon-sized, with Teflon-lined screw cap

(7) Toluene: Burdick and Jackson or equivalent grade

(8) Boiling Chips, Teflon: solvent rinsed

(9) Teflon Tape

(10) Disposable Aluminum Weighing Pans: approximately 2" in diameter, 1/2" deep; crimped sides; weighing approximately 1.0 grams

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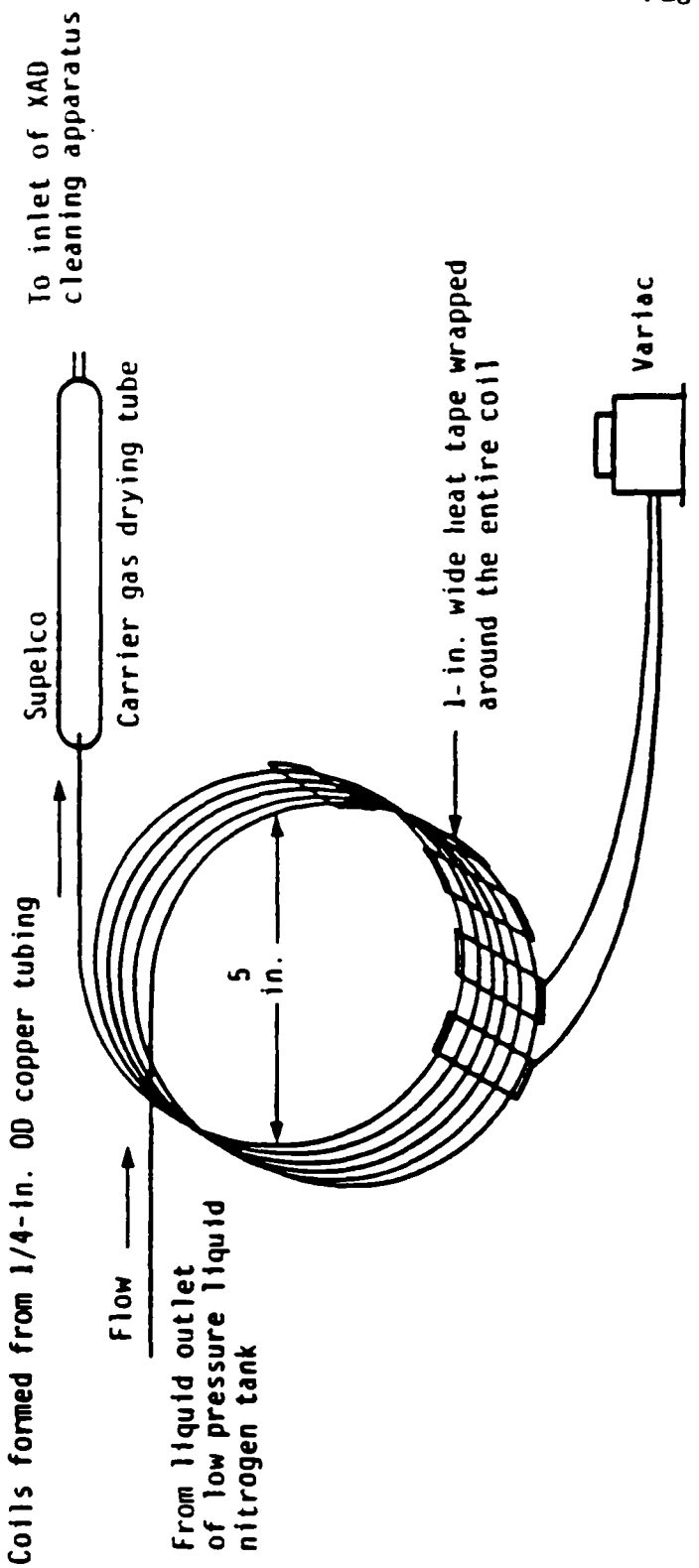

Figure 2. Heat Exchanger

1.8 Extraction Procedure

(1) Pour 7.5 kg of resin into a 24-gallon plastic garbage pail: cover pail. Add sufficient de-ionized water so that the entire resin bed floats. Allow it to soak for at least 7 days before proceeding.

(2) Transfer the resin-water mixture to the extraction apparatus by pouring it in the top. Drain the aqueous waste through the bottom valve into any suitable sized container. The aqueous waste is known to be non-hazardous and may be disposed of by pouring down a sink drain.

(3) Pour deionized water in the top of the extractor with the bottom drain valve open. Continue until the eluent is clear.

(4) Pour 4 gallons of methanol in the top of the extractor with the bottom drain open. Close the valve. The excess water will have been removed. Fill the resin bed with methanol. Replace the top cap. Allow it to soak overnight before proceeding.

NOTE: Redistilled, used Methanol may be used in this extraction step.

(5) Pump 5 gallons of methanol through the extractor over a period of 1.5 hour. Stop the pump. Close the inlet valve. Drain the bed through the bottom valve. Close the bottom valve.

(6) Change receiver vessels. Open the inlet valve. Pump 5 gallons of methylene chloride through the extractor over a period of 1.5 hours. Stop the pump. Close the inlet valve. Drain the bed through the bottom valve. Close the bottom valve.

NOTE: Redistilled, used methylene chloride may be used in this extraction step.

(7) Change receiver vessels. Open the inlet valve. Pump 5 gallons of new or redistilled methanol through the extractor over a period of 1.5 hours. Stop the pump. Close the inlet valve. Drain the bed through the bottom valve. Close the bottom valve.

(8) Change receivers. Open the inlet valve. Pump 5 gallons of new or redistilled methylene chloride through the extractor over a period of 1.5 hours. Collect the final 2 liters as 2 1-liter aliquots for the preparation of quality control (QC) samples. Stop the pump. close the inlet valve. Drain the bed through the bottom valve.

(9) Connect the heat exchanger to the liquid outlet of the liquid nitrogen tank. Connect the outlet of the liquid nitrogen tank. connect the outlet of the heat exchanger to the bottom valve of the extractor. Connect a Variac to the heat exchanger.

NOTE: Warming the extractor with an extra heat tape may speed up the drying process. The heated area should not be more than slightly warm to the touch.

WARNING

Do not exhaust the fumes directly into the room.

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(10) Turn on the Variac. Open the liquid nitrogen valve to a low flow. The N_2 flow should be the maximum flow that does not entrain resin. Adjust the Variac so that the output of the heat exchanger is gaseous nitrogen at a temperature somewhat above ambient (30-40°C is satisfactory). Continue until the resin is dry. This should take around 48 hours.

(11) Transfer the dried resin to brown glass solvent bottles, cleaned according to Level 1 procedures. Wrap Teflon tape around the cap.

(12) Store in an area free of organic materials.

2.0 QUALITY CONTROL ELEMENTS

2.1 Quality Control (QC) Checks

(1) Transfer the two 1-L aliquots of methylene chloride reserved in Step 7 of Section 1.8 to 2-L round-bottomed flasks. Add Teflon boiling chips. Add a pre-wetted Snyder column and adapter to each flask. In a hood, concentrate these QC samples to less than 100 mL. Transfer the concentrates, Snyder columns, and adapters to 500 mL round-bottomed flasks. Continue concentrating the QC samples to less than 5 mL. Cool. Transfer the concentrates to 10 mL volumetric flasks. Dilute to volume with fresh methylene chloride.

(2) Perform duplicate GRAV analysis using procedure AEERL/12 on each QC sample using 1 mL aliquots. Refer to AEERL/12, Standard Operating Procedure for Gravimetric Analysis of Organic Extracts, for details. Calculate the GRAV in units of mg GRAV material/sampling cartridge, where the 1-L methylene chloride AC sample is assumed to be equivalent to 8 sampling cartridges. The pass/fail value is 5 mg/cartridge.

(3) Perform duplicate TCO analysis on each QC sample. Refer to AEERL/13, Standard Operating Procedure for Total Chromatographable Organics, for details. Calculate the TCO in units of mg TCO material/sampling cartridge, where the 1-L methylene chloride QC sample is assumed to be equivalent to 8 sampling cartridges. The pass/fail value is 1.75 mg/cartridge.

(4) Perform a residual methylene chloride (RMC) test. Transfer 1.±0.1 g of dried, cleaned resin to a vial with a screw cap containing a Teflon-lined septum. Add 3.0 mL of toluene. Cap the vail and shake well. Analyze for residual methylene chloride by gas chromatography. Calculate the RMC as micrograms RMC/gram of resin. The pass/fail value is 1000 ug/g.

(5) The resin must pass all three tests before it may be used for sampling purposes. if it fails only the RMC test, redry the resin as described in Section 1.8 and retest for RMC as described in the previous step.

3.0 REFERENCES

1. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Editon), EPA 600/7-78-201, NTIS No. PB-293-795, pp. 26-32, 136-142 and Appendix B, October 1978.

2. Hammersma, J.W., D.G. Ackerman, M.M. Yamada, C.A. Zee, C.Y. Ung, K.T. McGregor, J.F. Clausen, M.L. Draft, J.S. Shapiro, and E.L. Moon. emission Assessment of Conventional Stationary Combustion Systems: Methods and Procedures Manual for Sampling and Analysis. EPA 600/7-74-0244, Appendix EO, January 1979.

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Page: 1 of 9

"RECOMMENDED OPERATING PROCEDURE FOR SAMPLE RECOVERY FROM XAD-2 RESIN BY PUMP THROUGH ELUTION"

by

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RECOMMENDED OPERATING PROCEDURE FOR SAMPLE RECOVERY FROM XAD-2 RESIN BY PUMP-THROUGH ELUTION

1. PROCEDURAL ELEMENTS

1.1 Scope and Application

This recommended operating procedure (ROP) has been developed as an alternative procedure to AEERL/22 for the recovery of semi-volatile organic samples collected on Amberlite XAD-2 resin. It has been shown to be applicable to the recovery of both ambient and source samples collected on XAD-2 resin.

This procedure has not been shown to be applicable to the recovery of samples collected on any other sorbent. It is applicable to the recovery of compounds soluble in methylene chloride or methanol. Caution must be used in the interpretation of analytical results where methanol was used in the workup since it is known to react with certain classes of compounds. Extraction solvent volumes and flow rates were developed for sampling cartridges used for IACP studies. Other cartridge designs may require different conditions.

1.2 Summary of Method

This procedure is basically a chromatographic technique. The sample is eluted from the resin by pumping solvent through the sample cartridge against the force of gravity. Depending upon purpose, one or more solvents may be used sequentially. The eluent is collected in one or more round bottom flasks and concentrated by solvent distillation using a Snyder column. Multiple sample cartridges may be manifolded for efficiency.

1.3 Personnel Requirements

This procedure requires one chemist or trained technician comfortable with solvent handling techniques. In addition, the person must have refined mechanical skills for fittings and glassware manipulation.

1.4 Facilities

This procedure requires one standard laboratory set up for organic sample analysis. This laboratory should include a fume hood, solvent storage, and sample storage. A source of glassware cleaned by AEERL Level 1 procedures is required. If flammable solvents are used, the laboratory should be free of sources of flames or sparks.

1.5 Safety Precautions

This procedure uses halogenated organic and/or flammable solvents. There are known hazards of poisoning due to inhalation, dermal exposure or ingestion and fire. There may be hazards due to longterm exposure to fumes from methylene chloride. The concentration step must be done in a fume hood or using some other form of vapor extraction. There are no known hazards due to contact with XAD-2 resin.

This procedure should be performed in a well-ventilated, no smoking area. Sources of sparks or flames should be removed from the area. Personal protection should include safety glasses, gloves, lab coats, and organic vapor mask. Disposable gloves should be worn during the manipulation of concentrated sample extracts unless all components of the sample are known to be non-hazardous.

1.6 Apparatus

(1) Extraction apparatus: see Figure 1

(2) Flask, Round Bottom, 2,000 mL with 24/40 ground glass joint

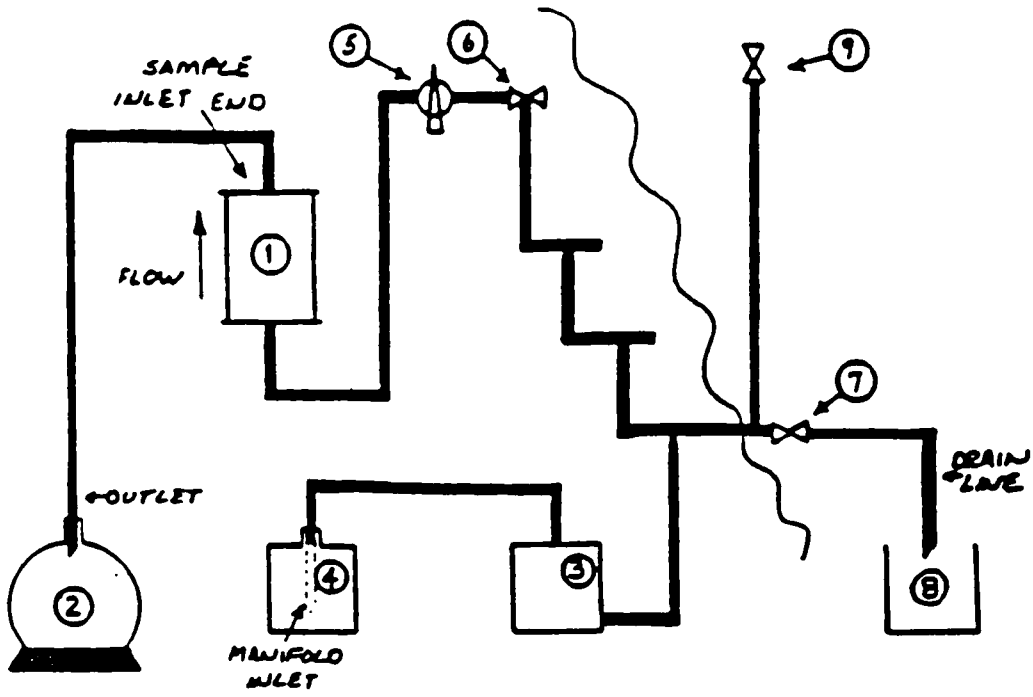
(3) Flask, Round Bottom, 500 mL with 24/40 ground glass joint

(4) Flask, Volumetric, 10 mL

(5) Autotransformer, variable: "Variac"

(6) 3 ball Snyder Column with 24/40 ground glass joint

(7) Heating Mantle, quartz: for 2000 mL RB



1. Sample Cartridge
2. Receiver-Round Bottom Flask
3. Pump
4. Solvent Reservoir
5. Vented-to-Atmosphere On/Off Valve
6. Flow Rate Controller Valve
7. Drain Valve
8. Drain Reservoir
9. Atmosphere Vent Valve

FIGURE 1. Diagram of Extraction Manifold

(8) Heating Mantle, quartz: for 500 mL RB

(9) Support Ring: for round bottom flasks

(10) Pump, variable speed: Teflon and stainless steel construction

(11) Squeeze bottle, Teflon

(12) Adapter: with 24/40 ground glass joint

(13) Syringe, glass, with luer lock fitting, 10 mL

(14) Glass wool

(15) Aluminum foil

1.7 Reagents and Supplies

(1) Methanol: distilled in glass or equivalent, dependent upon expected sample mass levels

(2) Methylene Chloride: distilled in glass or equivalent, depending on expected sample mass levels

(3) Pipet, Pasteur, disposable

(4) Bulb pipet, 1mL

(5) Boiling chips, Teflon; solvent rinsed

(6) Sample vials, 4 dram, glass: with screw cap and Teflon coated septum

(7) Filter units, .45 micron, disposable: to fit luer lock syringe, Supelco #5-8072 or equivalent

1.8 Extraction Procedure

Note: This procedure is written based upon sequential elution with $MeCl_2$ and MeOH of several manifolded samples in cartridges. This procedure may be used with a single solvent, dependent upon project requirements, provided that proper recovery of the desired sample components can be independently proven.

(1) Connect the sample cartridge to the manifold with the sample inlet up, if known (Refer to Figure 1). Place the manifold inlet into a reservoir of methylene chloride solvent (reservoir should contain 800 mL of sorbent/cartridge). Place the outlet into a 1 liter round bottom flask which is sitting on a support ring and labeled with the appropriate sample number.

(2) Close the drain valve. Open valves 5 & 6 for all lines. Turn on the pump. Adjust the regulating valve, 6, for approximately even flows to all cartridges. Adjust the pump speed to yield a flow rate of around 100-150 ml/minute through each branch of the manifold.

(3) Pump 500 mL, as measured in the collection flask, of methylene chloride through each cartridge. Close valve 5 for each cartridge as that amount is reached. Adjust pump as needed to maintain a flow of 100-150 ml/minute through each branch of the manifold. Because of the output vented to atmosphere feature of the valves, solvent in the resin dead volume (~250mL) will drain into the round bottom flask. However, it may be necessary to temporarily invert the cartridge or to disconnect the cartridge inlet to complete the drainage.

(4) When all the cartridges on the manifold have been pumped according to step 3, turn off the pump. Drain the manifold lines by opening the drain and the vent valve. Remove the $MeCl_2$ reservoir.

Note: Project requirements may call for a single solvent extraction. In this case, proceed from step 4 directly to Section 1.9, Sample Concentration.

(5) Close the vent and drain valves. Place the manifold inlet into a methanol reservoir. Place the outlet into a 2l round bottom flask sitting on a support ring and labeled with the appropriate sample number.

(6) Follow steps 2, 3, & 4 using methanol in place of $MeCl_2$.

Note: Project requirements may call for composited or combined extracts. If this is so, you may choose to elute the sample composite into a single 2 liter round bottom flask (or whatever size would be appropriate).

1.9 Sample Concentration

(1) Connect the large heating mantles to variacs in a fume hood.

(2) Drop some clean Teflon boiling chips into each flask. Place a round bottom flask containing extracted sample on each heating mantle. Place a pre-wetted Snyder column onto each flask. Add an adapter to the top of each column.

(3) Turn on the variac. Adjust the voltage so as to reflux the solvent. Concentrate the extract to less than 100 mL. Turn off the variac.

Note: It is beneficial to insulate the outside of the column with aluminum foil or glass wool.

(4) Transfer the concentrated extract to a 500 mL (or other appropriate size) round bottom flask, using additional solvent to quantitatively perform the transfer. Repeat the experimental setup of concentration steps 1 and 2 using small heating mantles and the 500 mL flasks.

CAUTION

The final concentration of the extracts calls for the exercise of judgement. It may not be possible to keep the extract of a high

solids sample, such as a source dilution sample, in solution if the total volume is reduced to 10 mL. If visual or historical evidence indicates that a given extract has concentrated enough for the analytical purpose of the sample, stop the process and dilute to a known volume in a volumetric flask.

(5) Turn on the variacs. Adjust the voltage so as to reflux the solvent. Concentrate the sample to less than 10 mL. Turn off the variac. Remove the adapter.

(6) Rinse the Snyder column with 1-2 mLs of the appropriate solvent into the round bottom flask. A clean Teflon squeeze bottle of solvent is adequate. Remove the column.

(7) Get a sample vial, a 10-mL volumetric flask or flask of appropriate size, a Pasteur pipet, a 10 mL luer lock syringe, a filter unit, and a Teflon squeeze bottle of the appropriate solvent.

(8) Remove the plunger from the syringe. Attach the filter unit to the syringe. Using a Pasteur pipet, transfer the concentrated extract to the syringe. Replace the plunger and filter the extract into the volumetric flask.

(9) Remove the plunger and use the same Pasteur pipet to transfer flask washes to the syringe. Again, replace the plunger and filter into the volumetric flask. Make up to exact volume with fresh solvent. Transfer to a sample vial. Seal with septum and cap. Wrap the cap joint with Teflon tape. Mark the vial with the sample code. Store in a refrigerator or freezer. Record the sample code, date of extraction, extraction solvent, and final volume.

Note: The extraction of a sample collected on XAD-2 with methanol frequently results in a cloudy extract due to resin

microparticulate. This microparticulate is innocuous as far as the sample preparation is concerned, though it does need to be removed before any analysis is performed on the extract. This microparticulate should not be confused with a saturated sample. The concentration step should not be cut short simply because microparticulate is present.

2. QUALITY CONTROL ELEMENTS

It is assumed that the sample set includes the desired quality control samples. If the sample set is not known to include a laboratory blank (it may be included as a blind sample, for example) one should be prepared as part of the sample set. No special procedure blanks are run. The blank value for this procedure is included in the XAD lab blank. The XAD lab blank is determined for each batch of XAD.

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(Please read Instructions on the reverse before completing)

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15. SUPPLEMENTARY NOTES AEERL project officer is Robert C. McCrillis, Mail Drop 61, 919/541-2733.

16. ABSTRACT The report gives results of an initial determination of differences in emissions when burning ordinary cordwood compared to kitchen cabinet making scraps. The tests were performed in an instrumented woodstove testing laboratory on a stove that simulated units observed in use at a kitchen cabinet manufacturer's facility. Three test burns were made, using a stove made from a 55 gal. (0.208 cu m) drum and a kit sold for that purpose. Test burn 1 used seasoned oak cordwood fuel, test burn 2 used particle board scraps, and test burn 3 used Formica-faced particle board scraps. The scraps for tests 2 and 3 were obtained from a kitchen cabinet manufacturer in Vermont. In general, the cordwood produced higher emissions of carbon monoxide and total hydrocarbons, while the composite woods produced higher emissions of the heavier molecular weight organic compounds. There were significant differences in burnrate between the tests, which introduced some uncertainty in interpreting the analytical results.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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